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Deliverable 4.2: Methodology for including specific biological effects and pathogen aspects into LCA

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NEPTUNE

New sustainable concepts and processes for
optimization and upgrading municipal wastewater
and sludge treatment

Contract-No. 036845

A Specific Targeted Research Project
under the Thematic Priority 'Global Change and Ecosystems'

Work Package 4 · Assessment of environmental sustainability and best practice

Deliverable 4.2 · Methodology for including specific biological effects and pathogen aspects into LCA

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1 Objectives of NEPTUNE WP4

The main objectives of NEPTUNE WP4 include:

- Complementation of state-of-the-art life cycle assessment (LCA) to cover specific biological effects (e.g. endocrine disruption) of micropollutants and pathogens.
- Applying the LCA methodology on a variety of waste water and sludge technologies in order to assess the environmental sustainability and best practices ranking list of
 - advanced waste water treatment for micropollutants and pathogens removal,
 - advanced nutrient removal control methods and processes and
 - options for sludge handling and treatment
- Formulate decision support guidelines based on LCA, cost/efficiency assessment and local constraints.

These objectives are sought fulfilled by performing the following tasks:

1. Development of “new” methodology
 - a. Defining overall methodological LCA framework in agreement with INNOWATECH
 - b. Developing methodology for including potential impacts of micropollutants and pathogens in the life cycle impact assessment (LCIA) of waste water treatment technologies. Results from whole effluent testing (WET) will be included.
2. Application of the LCA methodology including the “new” LCIA methodology suited for waste water treatment technologies
 - a. Providing and generating inventory data for the included waste water treatment technologies and sludge handling techniques
 - b. Estimating characterization factors (to be used for (eco)toxic impact potentials) for included emissions (e.g. of micropollutants and pathogens) on the basis of gathered effect and fate data, and the developed extended LCIA methodology
 - c. Modeling, running and interpreting the results of the LCAs on the included waste water treatments and sludge handling methods
3. Creation of a decision supporting guideline
 - a. Describing pros and cons for the different included waste water treatment and sludge handling techniques based on the results from the LCAs and cost/efficiency analysis

The present deliverable (D4.2) not only reports the results of task 1b, but also includes all the issues on new methodology as described in deliverable 4.1 (Larsen et al. 2007). Focus is on a new developed life cycle impact assessment methodology on toxicity (especially ecotoxicity) called EDIP 200X and special issues like whole effluent toxicity, endocrine disrupters, pathogens, land fill and normalization.

The other tasks are either already reported (Task 1a included in D4.1, Month 8) or included in future deliverables, i.e. task 2 and task 3 are included in deliverable 4.3 (month 40).

2 Introduction

As described in deliverable 4.1 (Larsen et al. 2007) NEPTUNE is using two main types of life cycle impact assessment (LCIA) methodologies when doing LCA studies on the waste water treatment technologies included. The basic methodology is the well known existing EDIP97 methodology (Wenzel et al. 1997, Hauschild and Wenzel 1998) for which the impact assessment on toxicity is PNEC based. However, in order to include the newest development on especially best available practice as regards ecotoxicity a new revised and updated EDIP 200X LCIA methodology has been developed. A first draft of this methodology is presented here. Furthermore, special issues related to waste water have been addressed by including novel development on LCIA methodology for possible impact from pathogens and whole effluent toxicity. Special focus is also allocated to micropollutants with specific toxic mode of action (i.e. endocrine disruptors) and the possibilities and relevance of including impact categories on land use and site-specific assessments have been addressed. Further, the special problems on how to deal with land fill and how to do normalization and weighting of impact potentials are also dealt with. The problem with possible bias in normalization references is especially addressed.

3 New LCIA methodology; EDIP 200X

When doing LCA studies on waste water treatment processes, and focusing on emission of micropollutants, the impact category covering aquatic ecotoxicity becomes very important. State-of-the-art and best practice methodology for LCA aquatic ecotoxicity impact assessment have recently been investigated and principles developed within OMNIITOX (Molander et al. 2004, Larsen and Hauschild 2007a, 2007b) and UNEP/SETAC (Rosenbaum et al. 2008), but only on chronic aquatic ecotoxicity and (yet) no normalization references exist. These principles are to a high degree integrated in the new LCIA methodology developed and described below.

The basic equation for a characterization factor (CF) for ecotoxicity related impact categories in EDIP97 has the following form (Wenzel et al. 1997, Hauschild et al. 1998b):

$$CF = f * BIO * 1/PNEC \quad (1)$$

In EDIP97 a CF is designated effect factor (EF, or equivalency factor) but this designation is in conflict with today's terminology within LCIA (see below), so in EDIP200X we will use the term characterization factor (CF) or ecotoxicity characterization factor (ECF).

The 'f' in equation 1 is a semi-quantitative fate factor designated *distribution factor* expressing the fraction of a given substance emitted ending up in a given end compartment (e.g. water or soil) given rise to potential exposure of the biota. 'BIO' is also a semi-quantitative fate factor designated *biodegradation factor* expressing the potential for biodegradation of the substance. The last component 1/PNEC, where PNEC is the Predicted No Effect Concentration, is an expression of the potential potency of effects on the biota. This type of factor is today typically designated 'effect factor' or 'ecotoxicity effect indicator (EEI)'

The fundamental structure of equation 1, i.e. the characterization factor being estimated on basis of the fraction ending up in the end compartment (fate factor, 'f'), a factor related to the potential time of existence in that compartment, i.e. potential time of exposure (disappearance or (bio)degradation factor, 'BIO') and a factor expressing the potential effect on the biota (ecotoxicity effect indicator, EEI), is maintained in the revision of the EDIP method described in the following sections.

It is important to notice that air is not considered as an end-compartment but only as a transient compartment with no exposure of/or effect on biota (only exception is human exposure via inhalation which is part of the impact category for human toxicity dealt with in Section 3.4). The included environmental end-compartments comprise freshwater (fw), marine water (mw) and soil (s). Only chronic effects (c) are considered except for direct emission to freshwater and marine water where acute effects (fwa, mwa) also are considered.

3.1 Fate

The revision of the fate modelling for a substance (i.e. micropollutant) emitted to the environment is described below.

3.1.1 Biodegradation (BIO)

EDIP97 exclusively uses **ultimate biodegradation** (i.e. full mineralization) in water as basis for the value of the biodegradation factor (BIO), see Table 3.1.

Table 3.1 Existing criteria for BIO in EDIP97

Criteria (EDIP97)	BIO
Readily biodegradable (meeting the 10-day window demand) OECD 301	0.2
Readily biodegradable (not meeting the 10-day window demand) OECD 301	0.2
Not readily but inherent biodegradable OECD 302	0.5
Not readily and not inherent biodegradable	1.0

As a consequence of the narrow range of possible values for BIO the difference in the weight of (bio)degradation in the estimation of CF is maximum a factor 5. The potential impact of very persistent toxic substances (e.g. dioxin) may therefore be seriously underestimated as compared to especially toxic but readily biodegradable substances (e.g. alcohol ethoxylates). Non-biodegradable substances, i.e. inorganics like metals, are all given BIO = 1.

Most other LCA methods use the **half-life (DT50)** as an indicator of degradation of the substance and typically differentiate between at least water and soil. In many cases it is however not known whether the DT50 value is expressing primary (bio)degradation (substance only transformed into another organic structure/product) or full mineralization.

For metals unrealistic high DT50 values have been seen in many cases, e.g. the UNEP/SETAC dataset (May 2006) the rate constant k equals $1.0E-20$ per second corresponding to a $DT50 = (\ln 2/k)/3600 \times 24 = 8.0E+14$ days = $2.2E+12$ years. This figure is identical to 2,200 billion years. In comparison the age of the earth and the rest of the solar system is generally considered as 4.55 billion years (<http://www.talkorigins.org/faqs/faq-age-of-earth.html>). So, in this case the half-life of metals is 'assumed' to be about 400 times longer than the age of the earth. The UNEP/SETAC dataset is used in this study in a revised version.

3.1.1.1 BIO for organic substances

In order to have a broader range of the BIO factor it is chosen to use DT50 in EDIP200X. By doing so we miss the knowledge about total mineralization of the substance and run the risk of not taking into account the possible significant persistence of transformed/metabolized substances which may be as toxic or more toxic than the parent substance. This problem is well known, also within risk assessment, and could at this stage of knowledge be dealt with by including known significant metabolites as separate substances. As most of the very persistent substances has a half-life at a level of 1000 days (Howard et al. 1991) and we want to keep BIO dimensionless at a level below 1 for the vast part of all substances we chose the following equation for BIO:

$$BIO = DT50/1000 \text{ days (dimensionless factor)} \quad (2)$$

If a measured DT50 is not available, then information on readily biodegradation/inherent biodegradation is used as shown in Table 3.2.

Table 3.2 New criteria for BIO if measured DT50 is not available

Criteria (EDIP200X)	DT50 (days)	BIO
Readily biodegradable (meeting the 10-day window demand) OECD 301	15 ¹	0.015
Readily biodegradable (not meeting the 10-day window demand) OECD 301	50 ¹	0.050
Not readily but inherent biodegradable OECD 302	150 ¹	0.150
Not readily and not inherent biodegradable	1000	1.000

¹ EC (2003a)

In case of no data on meeting the 10-day window demand BIO is set to 0.050 as default.

Temperature is an important factor for the degradation rate. Correction for differences in the temperature (T) used when measuring the DT50(t) and the temperature (X) chosen in the scenario maybe performed in the following way (TGD p. 49 equation 25, EC 2003a):

$$DT50(X^{\circ}C) = DT50(t) * e^{(0.08 * (T-X))} \quad (3)$$

As most standard tests on biodegradation are performed at 20 – 25 °C (e.g. OECD 301 and 302) and because we are dealing with relative comparison in LCIA we chose to use measured DT50 values at 20 – 25 °C directly for BIO. If non standard biodegradation data is used and they have been measured at a known deviating temperature, correction by use of equation 3 is recommended, e.g. if measured at about 12 °C a correction factor of 1/3-1/2 (0.4) is recommended.

3.1.1.2 BIO for inorganic substances, especially metals

For **metals** it is not possible to use a DT50 based on biodegradation as they are by definition not biodegradable. Assuming infinite (i.e. DT50 = 2.2E+12 years) exposure/bioavailability is causing unrealistic high weighting to the environmental impact from metals (as observed in other models using this approach) and may be considered as extremely conservative. However, several approaches dealing with persistence of metals related to bioavailability in a specific environmental compartment may be used (Skeaff et al. 2002, Paquin et al. 2005).

Looking at the **freshwater** aquatic compartment (pelagic) in the context of hazard assessment a review paper by Skeaff et al. (2002) suggests to use the partition half-life (of the bioavailable fraction) as a measure of persistence for metals, i.e. the half-life of the dissolved fraction of metals in the water column, the sediment acting as a sink. Based on existing knowledge (Skeaff al. 2002) this approach leads to average half-lives in freshwater of 10 – 30(50) days for many metals (Cr, Mn, Fe, Co, Cu, Zn, As, Sr, Se, Sn, Cs, Hg), for Cd about 100 days (10 – 250 days) and for Pb about 80 days (10 – 150 days) depending on depth in water column, season, suspended matter and more.

For the **marine compartment** (coastal area) the residence time of metals in the oceans may be used due to the fact that in principle at least all metals emitted to water (via water and air) will end up in the oceans sooner or later. The residence time (τ) can be defined as (Mackay 1991): $\tau = M/E$, where M is the amount in the compartment (e.g. kg in the ocean) and E is the inflow (or outflow, e.g. in kg/year) at steady state. The residence time may also be expressed as $1/k$, where k is the (flow)rate constant, which equals $\ln 2/DT50$. Therefore the residence time may be expressed as: $\tau = 1/(\ln 2/DT50) = DT50/\ln 2$. So, the half-life may be expressed as: $DT50 = \ln 2 * \tau$. Data on residence time is published in a number of studies (Sleeswijk 2005, Whitfield 1981) and is shown in Table 3.3 together with calculated half-lives in the upper 80 m or 100 m water column.

Persistent compounds in **soil** undergo a time dependent decline in bioavailability due to aging or sequestration, e.g. entangled in soil micropores or nanopores (Alexander 1999). This process is especially relevant for metals not undergoing any form of biodegradation. For metals the dominating factors for the extent of aging include soil pH, soil organic matter content, soil clay content, temperature, and drying and rewetting events (Daoust et al. 2006, Deschênes et al. 2005; Lock and Janssen 2003). These existing studies indicate that typically the higher the pH and the higher the organic matter content the higher the extent of aging. Unfortunately, residence time for the fraction of a metal being in a bioavailable state in a standard soil is not possible to derive from these studies but may become available if as suggested by these authors further research is performed. So, even though it seems reasonable to use the DT50 on bioavailability or aging when estimating BIO for metals emitted to soil this is not yet generally possible.

However, a very well done study on Cd bioavailability in soil by Hamon et al. (1998) may be used as a starting point. In this study the cadmium soil fixation rate (k) is estimated over a period of 27 – 47 years of phosphor fertilizer application (Cd contaminated) in an Australian clay loam soil, profile A1, 0-10 cm (lab. pH = 6 (field pH=6.5), $d = 1.4$ kg/L, cool temperate climate (Schafer 1980). The bioavailable fraction is assumed to be identical to the soil Cd available for the uptake by plants (in this case wheat) which according to the review by Lock and Janssen (2003) usually is correlated to the pore water metal concentration or salt solution extractable fraction typically considered as the soil metal bioavailable fraction. In the study by Hamon et al. (1998) the estimated Cd fixation rate is 1- 1.5% per year of total applied amount (as part of fertilizer) during 27 – 47 years assuming a first order reaction. If this rate is used the half-life of the Cd bioavailable fraction may be estimated as $DT50 = \ln 2/k$, where $k = 0.01 - 0.015$ per year resulting in a DT50 value of 46 – 59 years. The highest DT50 value (59) is corrected for background concentration.

The soil pH in the Hamon study (Hamon et al. 1998) is 6 and the standard soil pH we are aiming for has pH 7 pointing in a direction of more extensive fixation, i.e. a lower DT50 value. Further, Cd (and e.g. Pb) has a relatively high ionic radius as compared to e.g. Cu, Ni and Zn and therefore a slower aging as emphasized in the review by Lock and Janssen (2003). Anyway, as a very coarse approach a DT50 = 50 years may be used as a first preliminary value for metals in soil until better data becomes available.

Based on the approaches described above it may preliminary be recommended to use the following DT50-values when estimating BIO ($BIO = DT50/1000$ days) for metals, see Table 3.3.

Table 3.3 Preliminary half-life's for metals in different compartments

Substance	Freshwater (days)	Marine (days)					Soil (days)
	DT50 (partitioning) ¹	Total residence time ²	Total DT50	Residence time 80 m mixed layer ³	DT50 80 m mixed layer	DT50 100 m mixed layer ⁴	DT50 (aging)
Cadmium	100	156,950	108,800	37	25	25	18,250
Cobber	20	94,900	65,780	3,650	2,500	2,500	(18,250)
Zink	20	3,029,500	2,100,000	365	250	250	(18,250)
Nickel	-	63,350,000	43,910,000	7,300	5,100	5,100	(18,250)
Lead	80	124,100	86,020	1,100	760	760	(18,250)

¹ Skeaff al. (2002) ² Whitfield (1981) ³ Bruland (1980) ⁴ Estimated on basis of DT50 (80 m) by linear extrapolation

3.1.2 Distribution factors (f)

The main principle chosen here is that direct emissions to air are distributed between soil, freshwater and marine water as end compartments. Part of direct emission to water and soil are redistributed via air to freshwater, soil and marine water as end compartments if the substance has the potential of evaporating from the initial compartment. Further, part of the direct emissions to air will via soil (leaching and surface run-off) end up in freshwater (surface water) as end compartment and part of all direct emissions to freshwater will end up in marine water as end compartment. The EDIP97 methodology does not distinguish between freshwater (surface water) and marine water (salt water), and does not include surface run-off to freshwater via soil.

3.1.2.1 Factors for area of freshwater and soil, and inclusion of (coastal) marine water

Estimations based on most updated data from 2003 including data from 42 states (Europe and borderline states) of which 22 states include data on water land use (EUROSTAT 2006) result in an average **freshwater fraction** of the “land area” of 0.034. The regional ‘TGD’ model in EU generic risk assessment (EC 2003a, p. 88), only including freshwater and soil, uses an area fraction of 0.03 for freshwater. Defining, as typically, Europe as a subcontinent (i.e. borders: Arctic Ocean, Atlantic Ocean, Mediterranean Sea, Black Sea, Caucasus Mountains, Caspian Sea, Ural Mountains) results in a total **land area** of 10,390,000 km². The **marine area** relevant to be included in the Europe subcontinent scenario may be defined as shown in Table 3.4. Only half the area of the Mediterranean Sea (1,250,000 km²) is included as this marine area borders another continent, i.e. African continent. The same goes for the Black Sea (211,000 km²) bordering Turkey.

Table 3.4 Total land area of the European subcontinent and the proposed marine area to be included in the EDIP200X scenario

Region/Area	Total area (km ²)	Included in scenario (km ²)	References (accessed: 24-01-2009)
<i>Europe total land area</i>	<i>10,390,000</i>	<i>10,390,000</i>	http://en.wikipedia.org/wiki/Europe
Mediterranean Sea	2,500,000	1,250,000	http://en.wikipedia.org/wiki/Mediterranean_Sea
Black Sea	422,000	211,000	http://en.wikipedia.org/wiki/Black_Sea
English channel	75,000	75,000	http://www.britannica.com/eb/article-9109731
Irish Sea	100,000	100,000	http://www.britannica.com/eb/article-9368189?query=Irish%20sea&ct=
North Sea	745,750	745,750	http://www.internalwaveatlas.com/Atlas2_PDF/IWAtlas2_Pg157_NorthSea.pdf ; http://na.nefsc.noaa.gov/lme/text/lme22.htm
Baltic Sea	377,000	377,000	http://en.wikipedia.org/wiki/Baltic_sea
Coastal area	300,000	300,000	From Gibraltar to Nordkapp: 5000 km * 60 km. Estimated by authors
% marine area	30.3	22.7	

In Table 3.4 a rough estimate of a coastal area running from Gibraltar to Nordkapp (approximately 5000 km long) bordering the Atlantic Sea is suggested. The width is set to 60 km defined by the coastal zone relevant for commercial fishery, i.e. 80% of all fish consumed are caught within this zone.

If the width of the **coastal zone** is expanded to 250 km, i.e. equals the distance a particle freely following an eastern wind with a wind speed of 3 m/s (TGD value for regional model, p. 49, Table 12, EC 2003a) will reach in one day (average between two rain events, see Section 3.1.2.2), the fraction of marine waters becomes 27.8%. In comparison the average width of the continental shelfs are 80 km (average depth at edge 130 m). For Europe the narrowest shelfs are placed in south Europe (Spain and Portugal) and the widest along the Norwegian coast (http://en.wikipedia.org/wiki/Continental_shelf; http://www.soc.soton.ac.uk/CHD/classroom@sea/general_science/ocean_basins.html; http://www.esf.org/esf_article.php?language=0&activity=7&domain=3&article=127&page=1168, accessed: 22-06-2006)

Based on the analysis above the fraction of the marine area is set to ¼ of the total European subcontinent scenario area. Further, the fraction of freshwater is set to 0.03, leading to the recommended area fraction for EDIP200X shown in Table 3.5.

In the existing EDIP97 the area fraction for water is set to 0.5 (for Denmark) and 0.2 for Europe (Wenzel et al. 1997, Hauschild and Wenzel 1998)

Table 3.5 Recommended area fractions for EDIP200X

Area type	Area fraction	Symbol in EDIP200X
Freshwater	0.03	a
Marine water	0.25	b
Soil	0.72	(1-a-b)

3.1.2.2 Factors for emissions to air (f_a , $f_{sc(via\ air)}$, $f_{fwc(via\ air)}$, $f_{mwc(via\ air)}$)

For substances emitted to air the most important degradation process is reaction with photochemically generated radicals, especially OH-radicals (EC 2003a, p. 51) and therefore the $DT50_{air}$ is typically based on data from this process. In EDIP97 a very coarse approach is used for modeling fate in air, assuming that only substances with a $DT50_{air} > 1$ day contribute to potential impacts in the end compartments soil and water and in this case with the whole amount emitted. For EDIP200X it is suggested to estimate the amount that becomes deposited from the air as the amount left over after a dwell time equal to the median between to rain events (wet days). This new less coarse assumption assumes that an emitted amount will stay in the air compartment and undergo degradation until a rain event occurs which will lead to deposition (by wet deposition, i.e. rainout and washout) of the remaining amount on soil, surface water and marine water.

The degradation in air is typically described by a pseudo-first order equation as shown in equation 4, where the 't' included is the substance dwell time in air and "f" the fraction remaining.

$$f = e^{-(\ln 2/DT50_{air}) \cdot t} = 0.5^{(t/DT50_{air})} \quad (4)$$

However, the fraction of a substance associated (absorbed and/or adsorbed) to particles, i.e. being part of an aerosol, will not undergo degradation by photochemically generated radicals, only the gaseous phase will be attacked by the OH-radicals. The partitioning between aerosol and air (K_{XA} or K'_p) of semi-volatile organic chemicals may be expressed by the use of the partitioning between octanol and air (K_{oa}) as shown by Finizio et al. (1997). In its most simplistic form to be used for screening purposes the equation is as follows:

$$K_{XA} = 3.4 \cdot K_{oa} = C_P \text{ (mole/m}^3 \text{ particle)}/C_A \text{ (mole/ m}^3 \text{ air)} \quad (5)$$

Where C_P is the particle phase concentration and C_A is the gas phase concentration. K_{oa} may be determined as K_{ow}/K_{aw} , where K_{aw} is the air-water partitioning coefficient or the dimensionless Henrys law constant determined by $H/(RT)$:

$$K_{oa} = K_{ow} \cdot RT/H \quad (6)$$

K_{ow} is the octanol-water partitioning coefficient (dimensionless), R is the gas constant ($8.314 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the temperature (standard test: $25^\circ\text{C} = 298\text{K}$) and H is the Henrys law constant ($\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$).

The number of particles in (outdoor) air is typically measured as PM_x , i.e. particle matter with smaller diameter than $x \mu\text{m}$. PM_{10} covers the main part of the typically particles distribution (both number, surface area and volume) in both urban and rural areas (Seinfeld and Pandis 1997). In Europe the average PM_{10} levels are between $20 \mu\text{g/m}^3$ (northern Europe) and $50 \mu\text{g/m}^3$ (western Europe) and probably a bit higher in central and eastern Europe according to WHO's "Air quality guidelines for Europe" (WHO 2000). According to Seinfeld and Pandis (1997) a rural PM_{10} is around $20 \mu\text{g/m}^3$ and a remote continental PM_{10} around $10 \mu\text{g/m}^3$. For the EDIP 200X European scenario we chose an 'average' of $40 \mu\text{g/m}^3$. Assuming a density of 2000 kg/m^3 for the aerosols (Finizio et al. 1997) leads to a particle volume of $(40 \mu\text{g/m}^3)/(2000 \text{ kg/m}^3) = 2 \cdot 10^{-11} \text{ m}^3 \text{ aerosol/m}^3 \text{ air}$.

As we are aiming for the mass ratio in LCIA we have to correct for the differences in volumes of the two compartments, i.e. particle and air:

$$K_{XA} = 3.4 * K_{ow} * RT/H = (\text{Number of moles in particle}/2*10^{-11} \text{ m}^3)/(\text{Number of moles in air}/1 \text{ m}^3)$$

=>

$$((\text{Mass in particle}/\text{MW})/(\text{Mass in air}/\text{MW}))/2*10^{-11} = 3.4 * K_{ow} * RT/H \Leftrightarrow$$

$$(\text{Mass in particle}/\text{Mass in air})/2*10^{-11} = 3.4 * K_{ow} * RT/H \Leftrightarrow$$

$$\text{Mass in particle}/\text{Mass in air} = 2*10^{-11} * (3.4 * K_{ow} * RT/H) = k_{vol-ratio,p-a} * 3.4 K_{oa} = k_{vol-ratio,p-a} * (3.4 * K_{ow} * RT/H), \text{ where } k_{vol-ratio,p-a} = 2*10^{-11}$$

The recommended distribution (or fate) factor (f_a) for direct emission to air in air therefore becomes:

$$f_a = 0.5^{(t/DT50_{air})} * (1/(k_{vol-ratio,p-a} * (3.4 * K_{ow} * RT/H)) + 1) + (k_{vol-ratio,p-a} * (3.4 * K_{ow} * RT/H))/((k_{vol-ratio,p-a} * (3.4 * K_{ow} * RT/H)) + 1) \Leftrightarrow$$

$$f_a = 0.5^{(t/DT50_{air})} * (1/((k_{vol-ratio,p-a} * 3.4 * K_{ow} * RT/H) + 1)) + (1/(1 + 1/(k_{vol-ratio,p-a} * 3.4 * K_{ow} * RT/H)))$$

As $R = 8.314 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $T = 298\text{K}$, f_a becomes:

$$f_a = 0.5^{(t/DT50_{air})} * (1/((8,420 * k_{vol-ratio,p-a} * K_{ow}/H) + 1)) + (1/(1 + 1/(8,420 * k_{vol-ratio,p-a} * K_{ow}/H))) \quad (7)$$

The 't' included in equation 7 is the dwell time in air.

Mainly two deposition processes are determined for the dwell time of a substance in air, i.e. dry and wet deposition (MacKay 1991). Wet deposition is the predominant removal mechanism at least as regards particles at an altitude above 100 m (Seinfeld and Pandis 1997). So the "t" in equation 7 is here defined as the median between two rain events. The average number of rain days (> 0.1mm water) per year in Denmark in the period 1961 – 1990 was 172 days (Frich et al. 1997) and in the period 1931-1960 171 days (Cappelen and Juncher Jensen, 2001), meaning that on average the period between rain days in both cases was 2.1 days (365/172 and 365/171). In Europe (period 1931 – 1960, only France and Germany included) the average period between rain days was 2.5 days, estimated on basis of data from Cappelen and Juncher Jensen (2001).

It can therefore be expected that on average a period of about one day will last from a pulse emission until it will rain. It is here assumed that the fraction of a substance remaining after one day in the atmosphere will via rain (washout and rainout) end up in either surface water ($a = 0.03$) or marine water ($b = 0.25$) or soil ($1-a-b = 0.72$). Therefore:

$$f_{sc(via \text{ air})} = f_a * (1-a-b) \quad \text{where } a = 0.03 \text{ and } b = 0.25 \text{ (and } t = 1 \text{ day for } f_a \text{ in eq. 7)} \quad (8)$$

$$f_{fwc(via \text{ air})} = f_a * a \quad \text{where } a = 0.03 \text{ (and } t = 1 \text{ day for } f_a \text{ in eq. 7)} \quad (9)$$

$$f_{mwc(via \text{ air})} = f_a * b \quad \text{where } b = 0.25 \text{ (and } t = 1 \text{ day for } f_a \text{ in eq. 7)} \quad (10)$$

3.1.2.3 Factors for emissions to freshwater (f_{fwa} , $f_{a(via \text{ freshwater})}$, $f_{fwc(via \text{ freshwater})}$, $f_{sc(via \text{ freshwater})}$, $f_{mwc(via \text{ freshwater})}$)

For direct emissions to freshwater the distribution factor for acute toxicity remains 1:

$$f_{fwa} = 1 \quad (11)$$

For distribution factors regarding chronic toxicity in water the critical factors will be Henrys law constant (H), and the half-life in air as dealt with in the previous section (f_a). Henrys law constant (H) may be expressed as:

$H = (VP \cdot MW)/S$ where VP is the vapor pressure (Pa), MW is the molecule weight (g) and S is the water solubility (kg/m³) (EC 2003a, p. 45)

The molar distribution of a substance between air and water may be expressed as:

$$K_{air-water} = H/(R \cdot T) = C_{air} \text{ (mol/m}^3\text{)}/C_{water} \text{ (mol/m}^3\text{)} \quad (12)$$

Where R is the gas constant (8.314 Pa·m³·mol⁻¹·K⁻¹), T is temperature (standard test: 25°C = 298K) and C is the concentration (EC 2003a, p. 46).

If we as a rough approximation assume that equilibrium between water and air is achieved instantly and that the volume of freshwater corresponds to 3 m depth and that of air 1000 m height ("atmospheric mixing height", regional 'TGD' model default values, EC 2003a p. 88 table 12) the distribution will be:

$$K_{air-water} = H/(R \cdot T) = (\text{Number of moles in air}/1000)/(\text{Number of moles in water}/3) \Rightarrow$$

$$K_{air-water} = H/(R \cdot T) = (\text{Number of moles in air}/333.3)/(\text{Number of moles in water}/1) \Rightarrow$$

$$((\text{Mass in air}/MW)/(\text{Mass in water}/MW))/333.3 = H/(R \cdot T) \Leftrightarrow$$

$$(\text{Mass in air}/\text{Mass in water})/333.3 = H/(R \cdot T) \Leftrightarrow$$

$$\text{Mass in air}/\text{Mass in water} = 333.3 \cdot (H/(R \cdot T)) = k_{vol-ratio,a-fw} \cdot K_{air-water} = k_{vol-ratio,a-fw} \cdot H/(R \cdot T),$$

where $k_{vol-ratio,a-fw} = 333.3$

Substances emitted to freshwater (streams, rivers, lakes etc.) will sooner or later end up in marine water. If the freshwater residence time (t_{wrt} , 40 days) of the TDG regional model (EC 2003a, p. 88, Table 12) is used it may be assumed that on average it will take about 40 days for a suspended particle or inert substance to reach the sea in Europe. For simplification (ignoring differences in partitioning etc.) this figure may be used for all substances only including half-life as a parameter in this very coarse approach.

On this basis and taking equation 8, 9 and 10 into account $f_{a(via \text{ freshwater})}$, $f_{fwc(via \text{ freshwater})}$, $f_{sc(via \text{ freshwater})}$ and $f_{mwc(via \text{ freshwater})}$, becomes:

$$f_{a(via \text{ freshwater})} = (k_{vol-ratio,a-fw} \cdot K_{air-water})/(k_{vol-ratio,a-fw} \cdot K_{air-water} + 1) = 1/(1 + 1/(k_{vol-ratio,a-fw} \cdot H/(R \cdot T))) \Rightarrow$$

$$f_{a(via \text{ freshwater})} = 1/(1 + 1/(k_{vol-ratio,a-fw} \cdot H/(8.314 \cdot 298))) = 1/(1 + 1/(k_{vol-ratio,a-fw} \cdot H/2,480)) \quad (13)$$

$$f_{fwc(via \text{ freshwater})} = 1/((k_{vol-ratio,a-fw} \cdot H/(R \cdot T)) + 1) + f_{a(via \text{ freshwater})} \cdot f_{fwc(via \text{ air})} \Rightarrow$$

$$f_{fwc(via \text{ freshwater})} = 1/((k_{vol-ratio,a-fw} \cdot H/2,480) + 1) + f_{a(via \text{ freshwater})} \cdot f_{fwc(via \text{ air})} \quad (14)$$

$$f_{sc(via \text{ freshwater})} = f_{a(via \text{ freshwater})} \cdot f_{sc(via \text{ air})} \quad (15)$$

$$f_{mwc(via \text{ freshwater})} = f_{a(via \text{ freshwater})} \cdot f_{mwc(via \text{ air})} + f_{fwc(via \text{ freshwater})} \cdot 0.5^{(t_{wrt}/DT50_{freshwater})}, \quad (16)$$

where $t_{wrt} = 40$ days

3.1.2.4 Factors for emissions to soil ($f_a(\text{via soil})$, $f_{sc}(\text{via soil})$, $f_{fwc}(\text{via soil})$, $f_{mwc}(\text{via soil})$)

In the TGD regional model the mixing depth for natural soil and industrial soil is set to 0.05m (70% of total area) and that of agricultural soil 0.20m (EC 2003a, p. 88, Table 12). It is here chosen to use a weighted average of 0.1m.

Assuming that the solid fraction (i.e. particles) of soil in the EDIP scenario is covered with a water film leads to the consequence that substance/gas exchange with air is via water. The fraction of water in soil defined by the 'standard environmental characteristics' in the EC TGD (EC 2003a, p. 43 Table 5) is 0.2 m³ water per m³ soil. One square meter of soil with a depth of 0.1 m equals 0.1m³. Using the TGD standard value (0.2 m³/m³) results in a water volume of 0.02 m³ water in one square meter of soil with a depth of 0.1 m. As for emissions to water (see Section 3.1.2.3) the air volume above equals 1000 m³. The volume-ratio therefore becomes:

$$k_{\text{vol-ratio,a-s}} = 1000\text{m}^3/0.02\text{m}^3 = 50,000$$

The partitioning between solid phase (soil particles) and water phase (pore water) in soil may be described by K_d (L pore water/kg soil dry weight)

$$K_d = C_{\text{solid}} (\text{kg/kg dry soil})/C_{\text{water}} (\text{kg/L pore water})$$

As the density of dry soil may be set to 1.5kg/L (estimated on basis of 'standard characteristics' in EC 2000, p. 43 Table 5) the partitioning in soil may be expressed as:

$$C_{\text{solid}} (\text{kg/L dry soil})/C_{\text{water}} (\text{kg/L pore water}) = 1.5 K_d$$

As the volume fraction of solids in soil is set to 0.6 L/L soil and that of pore water to 0.2 L/L soil (EC 2003a, p. 43 Table 5) the equation becomes:

$$\text{Mass on solid}/0.6\text{L dry soil}/\text{Mass in pore water}/0.2\text{L pore water} = 1.5 K_d \quad \Leftrightarrow$$

$$\text{Mass on solid}/\text{Mass in pore water} = k_{\text{vol-ratio,s-pw}} * 1.5 K_d = 3 * 1.5 K_d = 4.5 K_d \quad (17)$$

Where $k_{\text{vol-ratio,s-pw}}$ equals 3 (0.6/0.2).

With the aim of simplification it may be assumed that it is only the amount present in the pore water that is relevant when looking at exposure of the soil biota (ignoring that pore water concentration is in at least restricted reversible equilibrium with the solid phase concentration). The fraction in the pore water may be expressed as:

$$f_{\text{pore water}} = 1/((k_{\text{vol-ratio,s-pw}} * 1.5 * K_d) + 1) = 1/(4.5 * K_d + 1) \quad (18)$$

For most organic substances (i.e. non- dissociating) K_d may be expressed as $f_{oc} * K_{oc}$ with a default value for f_{oc} of 0.02 (EC 2003, p. 43 Table 5):

$$f_{\text{pore water}} = 1/((k_{\text{vol-ratio,s-pw}} * 1.5 * f_{oc} * K_{oc}) + 1) = 1/((3 * 1.5 * 0.02 * K_{oc}) + 1) = 1/(0.09 * K_{oc} + 1) \quad (19)$$

If a measured value of K_{oc} is not available K_{oc} may be estimated by (EC 2003b):

$$K_{oc} = 1.26 * K_{ow}^{0.81} \quad (\text{predominantly hydrophobics})$$

For dissociating substances K_{oc} (based on the non-dissociating i.e. non-polar form of the substance) may be extrapolated to pH = 7 (the soil pH used in the EDIP scenario) by use of the substance acidity constant pK_a as in EDIP97 (Hauschild et al. 1998b):

$$K_{oc(pH=7)} = K_{oc(\text{non-polar})}/(1 + 10^{(pH-pK_a)}) = K_{oc(\text{non-polar})}/(1 + 10^{(7-pK_a)}) \quad (20)$$

For inorganics only measured K_d values may be used.

Based on these considerations combined with the same principles as described in Section 3.1.2.3 for emissions of organic substances to freshwater, $f_{a(\text{via soil})}$ becomes:

$$f_{a(\text{via soil})} = (1/(1+1/(k_{\text{vol-ratio,a-s}} * H/(R*T)))) * f_{\text{pore water}} = (1/(1+1/(k_{\text{vol-ratio,a-s}} * H/(R*T)))) * 1/(0.09 * K_{oc} + 1)$$

=>

$$f_{a(\text{via soil})} = (1/(1+1/(k_{\text{vol-ratio,a-s}} * H/2,480)))) * 1/(0.09 * K_{oc} + 1) \quad (21)$$

Where $k_{\text{vol-ratio,a-s}}$ equals 50,000

A part of the amount emitted to soil will end up in freshwater due to run-off with rainwater. In the TGD (EC 2003a, p. 88 table 12) it is proposed to use 0.25 as the fraction of rain water running off soil in the regional model. Further, it is assumed that annual precipitation amounts to 700 mm in the TGD (EC 2003a, p. 88 table 12). So, on one square meter soil the average every second day precipitation amounts to 3.8L (700L/(365days/2)) of which $0.25 * 3.8L = 1L$ will run-off and end up in surface water. Assuming that this one liter water achieves the same concentration as the soil pore water (20L per m² in the upper 0.1 m soil), which is mainly determined by the substance K_d -value (assuming that equilibrium is instantly and hence ignoring the kinetics of partitioning), the fraction ending up in surface water may be estimated. This very simple approach (ignoring time between rain-periods, particle transport etc.) leads to the following distribution factors:

$$f_{sc(\text{via soil})} = 1/((k_{\text{vol-ratio,a-s}} * H/(R*T)) + 1) * f_{\text{pore water}} + (f_{a(\text{via soil})} * f_{sc(\text{via air})}) - (1/((k_{\text{vol-ratio,a-s}} * H/(R*T)) + 1) * f_{\text{pore water}} * 1L/20L)$$

=>

$$f_{sc(\text{via soil})} = (1/((k_{\text{vol-ratio,a-s}} * H/(R*T)) + 1)) * f_{\text{pore water}} * 0.95 + (f_{a(\text{via soil})} * f_{sc(\text{via air})}) \quad \Rightarrow$$

$$f_{sc(\text{via soil})} = (1/((k_{\text{vol-ratio,a-s}} * H/2,480) + 1)) * (1/(0.09 * K_{oc} + 1)) * 0.95 + (f_{a(\text{via soil})} * f_{sc(\text{via air})}) \quad (22)$$

$$f_{fwc(\text{via soil})} = (f_{a(\text{via soil})} * f_{fwc(\text{via air})}) + (1/((k_{\text{vol-ratio,a-s}} * H/(R*T)) + 1)) * f_{\text{pore water}} * 1L/20L \quad \Rightarrow$$

$$f_{fwc(\text{via soil})} = (f_{a(\text{via soil})} * f_{fwc(\text{via air})}) + (1/((k_{\text{vol-ratio,a-s}} * H/2,480) + 1)) * (1/(0.09 * K_{oc} + 1)) * 0.05 \quad (23)$$

$$f_{mwc(\text{via soil})} = f_{a(\text{via soil})} * f_{mwc(\text{via air})} \quad (24)$$

If ecotoxicity effect data on soil organisms are used (only available in few cases) the data (expressed in mg/kg dry weight soil) have to be transformed as the equations above are based on pore water. Assuming a default density of dry soil: 1.5kg/L soil:

$$x \text{ mg/kg dry soil} = (x \text{ mg/kg dry soil}) * 1.5 \text{ kg/L} = 1.5 * x \text{ mg/L}$$

3.1.2.5 Factors for emissions to marine water (f_{mwa} , $f_{a(\text{via marine water})}$, $f_{fwc(\text{via marine water})}$, $f_{sc(\text{via marine water})}$, $f_{mwc(\text{via marine water})}$)

For direct emissions to marine water the distribution factor for acute toxicity will, as for fresh water, be 1:

$$f_{mwa} = 1 \quad (25)$$

For marine water it may be assumed that the upper mixing layer is 100 m deep (Whitfield 1981, Sleeswijk 2003) and that the "atmospheric mixing height" is 1000 m (regional 'TGD' model default values, EC 2003a p. 88 table 12). The volume-ratio therefore becomes:

$$k_{\text{vol-ratio,a-mw}} = 1000\text{m}^3/100\text{m}^3 = 10$$

Based on the same principles as described in Section 3.1.2.3 for emissions to fresh water $f_{\text{a(via marine water)}}$ and $f_{\text{mwc(via marine water)}}$ becomes:

$$f_{\text{a(via marine water)}} = 1/(1 + 1/(k_{\text{vol-ratio,a-mw}} * H/(R*T))) = 1/(1 + 1/(k_{\text{vol-ratio,a-mw}} * H/2,480)) \quad (26)$$

On this basis and taking equation 8, 9 and 10 into account $f_{\text{mwc(via marine water)}}$, $f_{\text{fwc(via marine water)}}$ and $f_{\text{sc(via marine water)}}$, becomes:

$$f_{\text{mwc(via marine water)}} = 1/((k_{\text{vol-ratio,a-mw}} * H/(RT)) + 1) + (f_{\text{a(via marine water)}} * f_{\text{mwc(via air)}}) \quad \Rightarrow$$

$$f_{\text{mwc(via marine water)}} = 1/((k_{\text{vol-ratio,a-mw}} * H/(2,480)) + 1) + (f_{\text{a(via marine water)}} * f_{\text{mwc(via air)}}) \quad (27)$$

$$f_{\text{fwc(via marine water)}} = f_{\text{a(via marine water)}} * f_{\text{fwc(via air)}} \quad (28)$$

$$f_{\text{sc(via marine water)}} = f_{\text{a(via marine water)}} * f_{\text{sc(via air)}} \quad (29)$$

3.2 Ecotoxicity effect

The ecotoxicity effect indicator (EEI) used in EDIP97 is a so-called no-effect indicator based on the Predicted No Effect Concentration (PNEC) founded in tiered risk assessment making use of conservative assessment factors. The main strengths of this approach are that it aims at protecting the most sensitive species of the ecosystem and that many existing chronic laboratory ecotoxicity test data is expressed as NOEC-values (No Observed Effect Concentration) on which PNEC is typically based.

As another core approach the EEI may be founded on effect-based indicators, like PAF-approaches (Potentially Affected Fraction of Species) based on Species Sensitivity Distributions (SSD's), making use of EC50 values (Effect Concentration affecting 50% of test species). The main strengths of the effect based approaches are that they don't suffer from the high uncertainty on determination of the NOEC value and further have the possibilities of being non-conservative which is important in the comparative framework of LCIA. Pros and cons of different EEI approaches have most recently been described by Larsen and Hauschild (2007a).

As a most reasonable choice for LCIA on ecotoxicity a linear HC50 PAF approach (Hazardous Concentration for 50% of species in an ecosystem, i.e. the concentration at which 50% of species having their EC50 exceeded) based on chronic EC50-values was chosen in the recently finished EU project OMNIITOX (<http://omniitox.imi.chalmers.se/OfficialMirror>). Due to data lack acute EC50 are used in most cases by including non-conservative assessment factors. This approach was mainly chosen due to the need for a best estimate when doing the comparison of the impact from different chemicals within the comparative framework of LCIA. The aim for best estimate was further strengthened by introducing data selection criteria, i.e. demands on standardization of ecotoxicity laboratory test conditions and species, and further including the 'bias-reducing' demand on averaging at trophic levels. This OMNIITOX approach is named GM-troph and described in details in Larsen and Hauschild (2007b).

For EDIP200X it is recommended to use the GM-troph method. The new ecotoxicity effect indicator for EDIP200X (substituting 1/PNEC) therefore becomes:

$$\text{EEI} = \text{GM-troph} = 0.5/\text{HC50}_{\text{EC50}} \quad (30)$$

The $\text{HC50}_{\text{EC50}}$ is estimated as the geometric mean of three EC50-values, one from each of the trophic levels primary producers (algae), primary consumers (crustacean) and secondary

consumers (fish). If more than one species represent the trophic level, the geometric mean within that trophic level is used as input EC50-value, see Larsen and Hauschild (2007b) for further details.

The EEI of the EDIP97 method (1/PNEC) is expressed in reciprocal of concentration, i.e. volume per mass (m^3/g). For the GM-troph this is almost the same, but the numerator is here expressed in units of PAF (which is actually a unit for fractions). So, GM-troph is expressed in PAF times volume per mass or $\text{PAF} \cdot \text{m}^3/\text{g}$. Ignoring the PAF part, GM-troph may be interpreted as a dilution volume, i.e. the volume needed for diluting one gram of the substance resulting in a concentration at which 50% of the ecosystem species are having their EC50 exceeded. In this way both the EDIP97 EEI and the EDIP200X EEI may be interpreted as a dilution volume but with two quite different endpoints, i.e. no (adverse) effect on the ecosystem and 50% effect on the ecosystem, respectively.

3.3 The EDIP200X ecotoxicity characterization factors

The basic structure of the EDIP200X ecotoxicity characterization factor (ECF) is as follow:

$$\text{ECF} = f * \text{BIO} * \text{EEI} = f * \text{DT50}/1000 * 0.5/\text{HC50} \quad (31)$$

In Appendix I is a summarization of the fate factors, i.e. the distribution factors and the BIO factor followed by equations for the different ECFs, and a list of definitions. In the appendix the numbering of the equations is continued from (32) to (45).

3.4 Human toxicity

The EDIP97 human toxicity impact characterization follows the same basic principles as the ecotoxicity impact assessment. The basic equation is however expanded to include exposure of humans (Hauschild et al. 1998a):

$$\text{CF} = f * \text{BIO} * 1/\text{NOAEC} * I * T, \quad (46)$$

Where:

NOAEC is No Observed Adverse Effect Concentration

I is the intake fraction, expressing the average daily intake of air, food, water etc.

T is the transfer factor, expressing transfer of a substance into the food chain of humans. For direct exposure, e.g. air or drinking water, it is 1.

The EDIP97 methodology on human toxicity is thoroughly described in Hauschild et al. (1998a). For the EDIP 200X methodology several changes are recommended:

- Changes of f as described in Section 3.1
- Using ED50 (dose where 50% is affected) instead of NOAEC
- Distinguishing between freshwater and marine compartment (e.g. in term of food intake)
- Minor changes in the transfer factors

The use of ED50 is implemented due to the fact that dose response curves are generally much steeper around the ED50 than for the low dose NOAECs, providing a less uncertain result and a more certain background for comparison. Since LCA is comparative and not for risk mitigation, the ED50 is better suited for the purpose. The exact derivation of ED50 for the range of substances included in EDIP 200X is given in Jolliet and Gold (2009).

Since a marine compartment has been introduced in EDIP 200X there should be a calculation routine for this.

The routine here is identical to the one used for freshwater until now, since it should be expected that the only exposure pathway is via seafood. Therefore a parallel fate-exposure and effect calculation for marine compartment is made.

The intake factors for seafood will be divided between seafood from freshwater and marine water, respectively in relation to their area fractions (0.03 and 0.25, see Table 3.5).

For the transfer factors the change in EDIP is a replacement of the earlier SCF (Stem Concentration Factors) with a TSCF (Transpiration Stream Concentration Factors). The expression for SCF (now TSCF) in EDIP 200X is thus reduced to

$$TSCF = \frac{0.314 \times \exp \left[-\frac{(\log K_{ow} - 1.78)^2}{2.44} \right]}{0.1} \quad (47)$$

An additional change is made in the transfer factors for beef and milk since it is recommended to truncate logKow at 6.5, i.e. for logKow values above 6.5 logKow is assumed to have the value 6.5.

3.5 Normalization references for the EDIP 200X ecotoxicity-related impact categories

In the context of LCA, though the normalization step is stated as optional in the ISO Standards (ISO 14044:2006), it is commonly used in order to put into perspective the impact assessments and to ensure consistent interpretations. The principle is to divide each impact potential by its relative magnitude for one person in one year within the defined geographical scope of the impact. Normalization results are thus expressed in a single unit – Person Equivalent (PE) – for all impacts, allowing therefore comparisons between each other.

In the present study a first draft on normalization references for EDIP 200X is presented and only normalization references for the ecotoxicity-related impacts are included. They are calculated for the reference year 2004, due to availability of required data. The geographical scope of the study is limited to Europe as a continent (though emission data do not include all the European countries, most of them (35) are represented).

Overall, used emission data are allocated among the different assessed countries and normalization references is calculated at a national scale (no spatial differentiation is included in the methodology itself). However, emission data quality varies significantly from one country to another. Consequently, large uncertainties might be underlying with some of those assessments and it is recommended to privilege the normalization references set for Europe as a continent. Country-sized assessments should rather be considered as rough indicators for potential deviations in the context of a sensitivity analysis (only based on emission data variations).

With respect to the normalization references for Europe, it turned out that few compounds out of the full inventory are responsible for most of the total impact potentials, namely metals such as copper or zinc, tributyltin, and pesticides, like lambda-cyhalothrin or betacyfluthrin. Unfortunately, some of these chemicals are associated with a poor quality of emission data and, therefore, large uncertainties are related to the presented results. Furthermore, the results might also be biased: because of the availability of emission data, only a small part of the 2 000 compounds, for which characterization factors have been estimated, was assessed and results tends to show that a potent chemical, even though poorly reported, might turn out to play a significant role in the impact assessment.

Thus, it is highly recommended to update the normalization references as soon as emission data can allow better consistency (representativeness of the actual emissions), completeness (among the assessed countries as well as in the amount of assessed chemicals) and reliability (for all data sources).

The following impact categories are included:

- Acute ecotoxicity in aquatic environment: ETWA,
- Chronic ecotoxicity in aquatic environment (freshwater): ETFWC,
- Chronic ecotoxicity in marine environment: ETMWC,
- Ecotoxicity in terrestrial environment: ETSC

3.5.1 Characterization factors

Based on the work and substance data of the UNEP/SETAC project (Rosenbaum et al. 2008), characterization factors (CFs) were estimated for more than 2 000 organic and inorganic substances for the four impact categories, except ETMWC for which only the substances included in the normalization reference is allocated CFs until now.

Heavy metals were characterized without any speciation. A mass balance (molecular weight) was performed to obtain the characterization factors for each heavy metal as a single compound. Same methodology was applied to tributyltin, which was assessed as tributyltin fluoride (with mass correction):

- As data for characterization factors regarding the free ion heavy metals are not available, it has been chosen to use data on complexes (mainly chloride as ligand) and to weight by the mole mass (M_w) ratio: $M_w(\text{complex})/M_w(\text{metal})$.
- Same procedure was applied for tributyltin (TBT), for which the characterization factor relevant data is not available. Therefore, it has been chosen to use data for TBTF (tributyltin fluoride), weighted by the ratio $M_w(\text{TBTF})/M_w(\text{TBT})$.

3.5.2 Emissions data

Emission data were gathered based on the framework of previous assessments carried out for the EDIP-methodology (Hauschild and Wenzel 1998). Those data are then distinguished into several categories presented in Table 3.6. Their inclusion in the different assessed impacts is also notified.

3.5.3 Inventory

Search for data on micropollutants regarding waste water emissions to freshwater on a European level gave no useable results. A request to the European Environment Agency (EEA) gave the following answer (Jacobsen 2009): *“Concerning data across Europe for emissions on hazardous substances, I can say that at present we do not have such data sets at the EEA. We are, however, aware that some assessments have been made either nationally or by some of the international conventions (HELCOM, OSPAR, River Danube, etc.). Therefore, a reporting request is in preparation to be launched this fall to get an overview of such data available for specific hazardous substances. Most likely, these data will be more abundant for priority hazardous substances relating to the Water Framework Directive than for emerging pollutants, such as pharmaceuticals. This reporting takes place via the European Topic Center for Water as part of the framework contract with EEA. Results will be reported as aggregated to levels of River Basin Districts or sub-units hereof, depending on the structuring of the data in the member countries. Results will be available in*

2010 at the earliest. As another source of information concerning emissions to surface water of hazardous substances is the EMPODAT database created during the NORMAN project. More info on this at: <http://www.ei.sk/norman/empodat/>. As I have understood, the EMPODAT database is now operated on a membership basis so to which degree data are available to other EU funded projects like NEPTUNE I do not know."

Apparently the EMPODAT database does not include an overview of waste water emissions and only data suppliers have access.

As shown below and in Table 3.6 inventory data for waste water emissions are therefore based on data from OSPAR and HELCOM in combination with a comprehensive Dutch study (Van der Auweraert et al. 1996) and modeling according to the EDIP200X fate part.

Each emission category has been assessed separately and they are reported below as such.

Table 3.6 Assessed substances associated with their data sources

Assessed groups of substances	ETWA	ETFWC	ETMWC	ETSC	Data sources
Heavy metals in waste water (Hg, Cd, Pb, Cu, Zn)	X	X	X		<ul style="list-style-type: none"> - OSPAR (2006a) for the North Sea/Atlantic Ocean - HELCOM (2007) for the Baltic Sea
Organics in waste water	X	X	X		<ul style="list-style-type: none"> - Van der Auweraert et al. (1996) (extrapolated)
Oil compounds (off-shore plants and refineries)	X		X		<ul style="list-style-type: none"> - OSPAR (2006b) and CONCAWE (2004) (EEA (2007)) - Fingas and Fieldhouse (2004) and Potter and Simmons (1998) for speciation
TBT compounds (antifouling paints...)	X		X		<ul style="list-style-type: none"> - DEPA (1997); extrapolations using sea areas from Table 3.4
Atmospheric depositions (heavy metals, PAH, dioxins, HCB, PCB)		X	X	X	<ul style="list-style-type: none"> - EMEP/CEIP-database for emissions (year 2004)
Pesticides		X		X	<ul style="list-style-type: none"> - DEPA (2006) for speciation - EUROSTAT-database (year 2008) for consumptions; OECD (2008a) and EEA (2004) for sales. - EUROSTAT (2002) for active ingredients (a.i.) properties - Emission factors from Hauschild and Wenzel (1998) and from Birkved and Hauschild (2006)
Sludge				X	<ul style="list-style-type: none"> - EUROSTAT-database (year 2003), OECD (2008b) for emissions. - Compositions from Tørsløv et al. (1997)

3.5.3.1 Heavy metals in waste water

Data collection for heavy metals is mainly the combination of two sources: OSPAR (2006a) and HELCOM (2007), which cover the marine area of the Atlantic Ocean and all the northern seas (North Sea, Baltic Sea...). As evident from above only data regarding inputs to the seas are reported in a relatively comprehensive way today. Therefore, a number of extrapolations were required in order to get a clear cut between emissions to freshwater and discharges to marine environments (in order to assess ecotoxicity in both freshwater and marine ecosystems). As illustrated in Figure 3.1, three points of releases are defined:

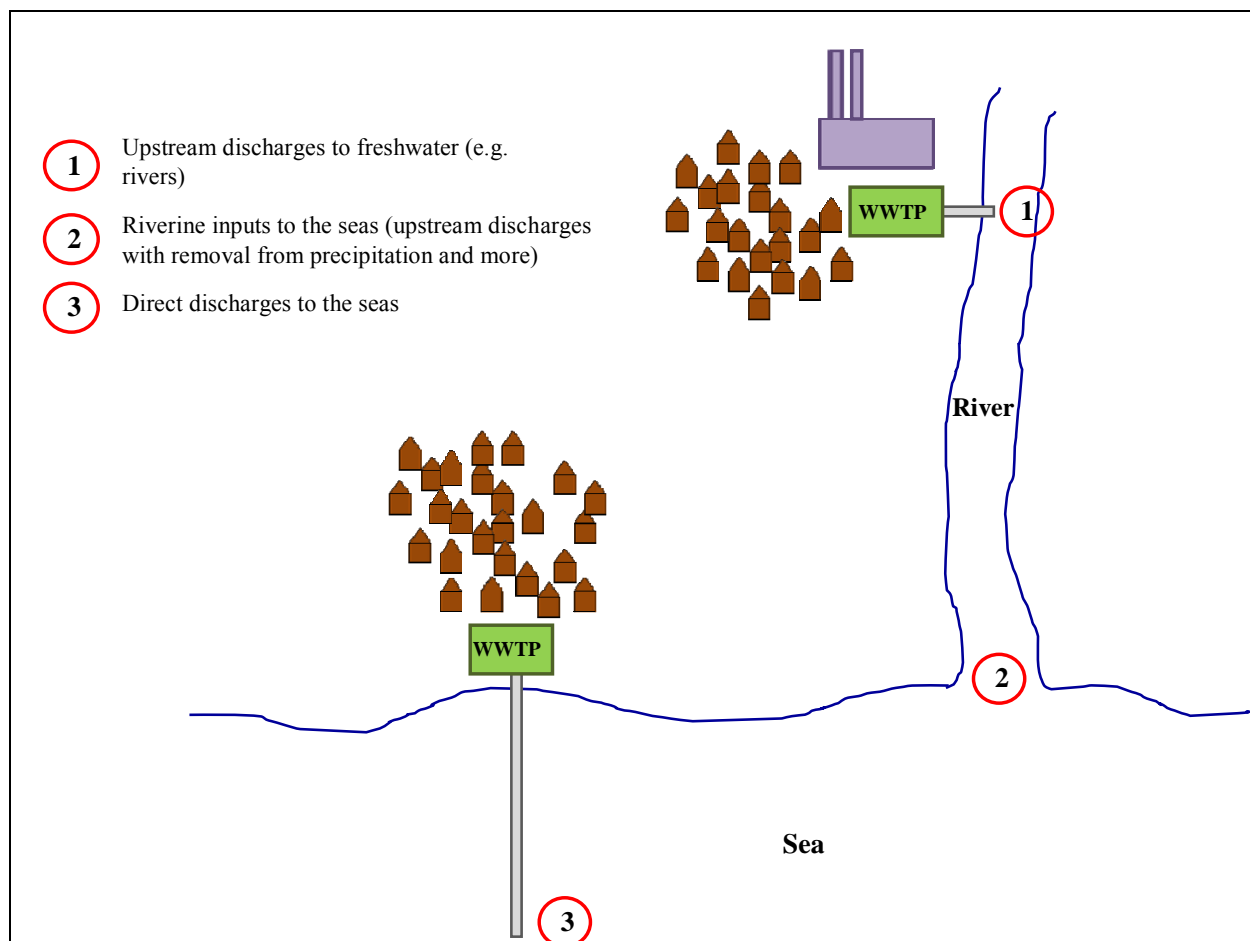


Figure 3.1 Illustration of model distinguishing between releases to freshwater and marine water

Point 1: discharges to freshwater

As no usable data are available to quantify consistently the direct emissions to freshwater ecosystems these emissions were derived from the riverine inputs to the seas (point 2), reported by OSPAR (2006a) and HELCOM (2007). This was done by adding the removal from precipitation occurring in the river, when the metals are carried to the coastal areas. The removal part was estimated according to the EDIP200X model, i.e. see Section 3.1.1.2 and 3.1.2.3, assuming a first-order differential equation, with a time of 40 days to reach the coasts after release and considering the half-lives of each of the concerned heavy metals (100 days for Cd, 80 days for Pb, and 20 days for Cu, Zn, and Hg).

Point 2: riverine inputs to the seas

Raw data for the riverine inputs are provided by OSPAR (2006a) and HELCOM (2007). Theoretically they consist of the discharges to freshwater (point 1) with deduction of the part of metals removed when conveyed in the river (or other freshwater system). As these data do not encompass all European countries, extrapolations by use of gross domestic products (GDP) were performed to get discharges of heavy metals for all European countries (see below).

Point 3: direct discharges to the seas

Part of the waste water is directly released to the seas when the waste water treatment plants are located nearby the coasts. OSPAR (2006a) and HELCOM (2007) report those specific emissions for some European countries. Obviously, this category of releases refers

only the countries with a coastline. Extrapolations using coastal gross domestic products (coastal GDP) were carried out to fill gaps in the reporting countries (see below).

Extrapolation

As mentioned above, extrapolations were performed to fill gaps in the data for some European countries. They consist of:

- Minor lacks are associated with data for Denmark, since no emissions are reported for inputs to the North Sea, as well as for Portugal (no information for releases of Hg). In the first case, the same allocation as for nutrient loadings (nitrogen, phosphorus) to the Baltic Sea and to the North Sea for Denmark (73% and 27%, respectively) was used, given that the loadings of metals to the Baltic Sea was known. For Portugal, linear indexations on Spanish emissions were performed to get releases of mercury.
- Reported riverine inputs to the seas from OSPAR (2006a) and HELCOM (2007) only concerns northern countries (and part of Spain). Therefore, discharges of heavy metals from European countries ending up in the Mediterranean Sea and the Black Sea are missing. Based on the reported data for the northern countries, extrapolations to get riverine inputs for each southern and central European country were performed using gross domestic products (UN 2009; cf. Appendix II).
- As for data about the riverine inputs to the seas, a number of gaps are also associated with reported direct discharges to the seas. Coastal gross domestic products (coastal GDP) were calculated, based on coastal gross domestic products per capita (person) and coastal population densities for the concerned countries (EUROSTAT 2009). Those coastal GDP were used to extrapolate from the basis of reported countries to all coastal European countries (see Appendix III for further details).

Thus, the inventory for freshwater ecotoxicity (ETFWC) includes the discharges to freshwater environment (point 1), whereas the inventory for assessing marine ecotoxicity (ETMWC) includes direct discharges to the seas (point 3) as well as the riverine inputs to the seas (point 2). The inventory for acute ecotoxicity in aquatic ecosystems encompasses the direct discharges to the seas (point 3) as well as the releases to freshwater environment (point 1).

Emission data can be viewed in Appendix IV.

3.5.3.2 Organic compounds in waste water

As mentioned above it has not been possible to find organic inputs to aquatic ecosystems for the year 2004. However, a large study performed in the Netherlands (Van der Auweraert et al. 1996) has been used as a proxy, assuming no change over time (no delocalization or closure of concerned industries and no change in the emission loadings).

The same procedure as for discharges of heavy metals via waste water was used to estimate the emissions of organics for all three points of inputs (depicted in Figure 3.1). First, an apportionment was performed to separate direct emissions and riverine inputs to the seas: the ratio between the coastal GDP and the overall GDP of the Netherlands was used (see Table 3.7).

Table 3.7 GDP apportionment for the Netherlands (year 2004)

2004	GDP (€)	%	Source
GDP coastal	8.75E+10	18%	EUROSTAT (2009) ; see Appendix III
GDP inland	4.04E+11	82%	
GDP overall	4.91E+11	100%	EUROSTAT-database (year 2004)

Thus, based on Table 3.7, 18% of the emissions in the Netherlands are assumed to go directly to the sea, whereas 82% are assumed to be discharged directly into the freshwater environment (e.g. rivers and lakes).

Direct inputs to the seas (point 3 on figure 1) were then extrapolated to all coastal European countries, using the coastal GDP (cf. Appendix III). Releases to freshwater environment (point 1 on figure 1) for all European countries were also derived from the Dutch ones, using the overall GDP. From those discharges in freshwater environment, the inputs to the seas (point 2 on figure 1) were calculated, considering, as for the heavy metals, a first order removal (in this case degradation) with an average time of 40 days to reach the seas and specific half-lives for each concerned organics (see Table 3.8).

Table 3.8 Half-lives (DT50) for organic substances included in the assessment

	DT50 (days) ¹
Benzene	7.1
Benz(a)pyrene	70.8
Ethylbenzene	22.9
Fluoranthene	70.8
Isopropylbenzene	22.9
Toluene	22.9
Xylenes	15.0
1,2-Dichloroethane	70.8
Hexachlorbutadiene	180.0
Hexachlorcyclohexane	180.0
Tetrachlorethylene	70.8
Tetrachlormethane	120.0
1,1,1-Trichloroethane	120.0
Trichloroethene	70.8
Trichloromethane	70.8
Vinyl Chloride	22.9
Chlorobenzene	70.8
Hexachlorobenzene	2291.7
PCB	180.0
Pentachlorophenol	22.9
Trichlorobenzene	120.0

¹ Based on data from the UNEP/SETAC USETox database (Rosenbaum et al. 2008)

Thus, as for heavy metal emissions via waste water, the inventory for organics regarding freshwater ecotoxicity (ETFWC) includes the discharges to freshwater environment (point 1 on figure 3.1). The inventory for assessing marine ecotoxicity (ETMWC) includes direct discharges to the seas (point 3) as well as the riverine inputs to the seas (point 2). The inventory for acute ecotoxicity in aquatic ecosystems (ETWA) encompasses the direct discharges to the seas (point 3) as well as the releases to freshwater environment (point 1).

3.5.3.3 Oil discharges

This category is only assessed for ecotoxicity in the marine environment (due to availability of data).

Oil discharges have been documented for two emission sources: refineries and off-shore plants. Data for refineries refer to the year 2000, but small differences are expected with 2004. Spills occurring at off-shore stations (data for 2004) constitute the major part of the total discharges (> 90%). Generally, accidental emissions are not to be included for normalization references; therefore accidental spills have not been included here.

It must be emphasized that the considered data only cover emissions occurring in the North Sea, as it has not been possible to find relevant data sources for other European marine areas. No extrapolation was performed.

Oil emissions have been expressed as inputs of single compounds to the marine ecosystems, using an average crude oil composition, though crude oil composition can vary a lot, particularly depending on the extraction location (Fingas and Fieldhouse 2004). The distribution by chemical groups (Fingas and Fieldhouse 2004) was combined with a partial speciation by substances as reported by the "Total Petroleum Hydrocarbon Criteria Work Group" (Potter and Simmons 1998). Overall it was assumed that:

- The effects of the included compounds are additive (as typically assumed in LCIA).
- Only saturates and aromatics were assessed (representing 80.56% (Fingas and Fieldhouse 2004) of the total composition). Due to lack of composition data, resins and asphaltenes were excluded.

Only substances, for which characterization factors are available in the EDIP 200X database, have been assessed. They represent 32.3% of the total emissions by weight. Due to large differences of toxicity among the compounds, no extrapolation would have proved to be consistent, and consequently, the remaining part of the substances is not assessed.

Furthermore, for data availability reasons, emissions could not be consistently allocated for each European "source-countries"; therefore, the assessment of oil compounds is only made for the full Europe.

Background data, containing the speciation of an average crude oil, are supplied in Appendix V.

3.5.3.4 Organotin compounds

This category is only assessed for the ecotoxicity in the marine environment due to data availability.

No complete data have been found concerning organotin emissions. Therefore, the emission data are only based on estimates of organotin releases for Denmark (DEPA 1997). These emissions have been extrapolated to Europe based on sea areas. Estimations of sea areas for Europe are presented in Table 3.4 and also shown in Appendix VI.

Due to low data availability, no apportionment among the European countries has been made and, therefore, the impact of organotin is only assessed on a whole Europe scale.

Appendix VI depicts input data and the potentials for organotin compounds for ETWA and ETMWC.

3.5.3.5 Atmospheric deposition

Generally, air emissions are much more monitored than water-borne discharges. Emissions of heavy metals and dioxins are rather well reported by countries in the framework of the EMEP Programme (EMEP/CEIP-database). To fill gaps for some countries, expert estimates provided by the EMEP Status reports (Gusev et al. 2008, Ilyn et al. 2008) have been used for Cd, Hg, Pb, hexachlorobenzene (HCB), polychlorobiphenyls (PCBs) and poly-aromatic hydrocarbons (PAHs); for the remaining missing data, extrapolations using GDP have been performed. Appendix VII summarizes the emission data by country with respect to their reported, estimated or extrapolated characters.

3.5.3.6 Pesticides

Pesticide use was assessed using a speciation profile, based on the agriculture in Denmark. In the present study, the use was assumed to equal the consumptions within the considered year. A detail of all the active ingredients consumed in Denmark in the year 2004 was documented by the Danish Environmental Protection Agency (DEPA, 2006). It lists over 207 substances, which are then assessed separately using, when available, the EDIP 200X characterization factors.

As described in Hauschild and Wenzel (1998), it is assumed that 15% of the applied pesticides are not taken up by plants, thereof is 10% assumed to reach the agricultural soil and 5% is assumed to reach the surroundings by air. Here, the agricultural soil itself is considered as part of the technosphere and therefore not accounted for in the assessment. However, a part of the 10% reaching the soil ends up either in groundwater or in the (surface) freshwater ecosystems (run-off and via drainage system), which is part of the biosphere, and therefore accounted for in the inventory for assessing ecotoxicity in aquatic ecosystems (only ETFWC is considered here). So, here it is assumed that 0.1% of the total consumptions of active ingredients will reach the freshwater ecosystem. However, as both the study by Birkved and Hauschild (2006) and Linders et al. (1994) indicates that at least as much as 1% of the total active ingredient consumption may end up in freshwater this figure is used in a sensitivity analysis (see Section 3.5.5.2).

Thus, to summarize, the inventory for terrestrial ecosystems (ETSC) consists of emissions of active ingredients to air (5% of total consumption; only the fraction depositing on soil in the surroundings), while the inventory for assessing ecotoxicity in freshwater ecosystems (ETFWC) encompasses emissions of active ingredients to air (5% of total consumptions; only the fraction depositing on fresh water) and run-off or via drainage system to freshwater ecosystems (0.1% of total consumption).

Following the typical reporting rules in the inventories, pesticides were divided into four main categories: fungicides (F), herbicides (H), insecticides (I) and other pesticides (e.g. growth regulators). Each active ingredient was then distributed within those classes, using the work from EUROSTAT (2002). Extrapolations from Denmark to Europe were performed using the consumptions of each of the four classes of pesticides for each country. Consumptions refer to the base year 2003 (EUROSTAT-database), but only minor changes are expected regarding the situation in 2004. A few countries did not report pesticide consumptions: for those cases, sales in previous years were used instead.

Only substances, for which the characterization factors are available in the EDIP 200X database, were assessed. They represent 82% of the total emissions (in weight). As for the inventory of oil discharges, due to large differences of toxicity among the compounds, no extrapolation would have proved to be consistent and, consequently, the remaining part of the substances is not assessed.

The background data are documented in Appendix VIII.

3.5.3.7 Sewage sludge applied to agriculture

Some toxic substances end up in soil, via sewage sludge applied to agriculture. The total loadings of sewage sludge applied to agriculture by country in 2004 (EUROSTAT-database, year 2008; OECD 2008a) were specified, using the composition of the sludge from Tørsløv et al. (1997).

Nota: For Denmark, 2002 is the latest reported year for sewage sludge use (OECD, 2008). It is assumed that this use does not vary significantly with the situation in 2004.

3.5.4 Results

Normalization references are documented for 35 countries for each of the four assessed impacts. They must not be considered as site-dependent as they only differentiate through emission data and not via the impact assessment methodology.

As mentioned above background data can be found in the appendices.

3.5.4.1 Acute ecotoxicity in aquatic ecosystems

The substances contributing to the normalization references (i.e. impact potentials) for ETWA are presented in Table 3.9 and the values for the normalization references in Table 3.10.

Table 3.9 Substances contributing with 0.2% or more to the total impact potential (IP) for ETWA

Substances	Fraction of IP
TBT	37.4%
Cu (via waste water)	29.1%
n-octane (oil discharges)	18.9%
Zn (via waste water)	10.7%
Fluoranthene (via waste water)	1.8%
Pb (via waste water)	0.5%
Hg (via waste water)	0.4%
Benz(a)pyrene (via waste water)	0.3%
Cd (via waste water)	0.2%
<i>Total</i>	99.2%

The normalization reference for *acute ecotoxicity in the aquatic environment* is dominated by TBT (37%), copper from waste water (29%), and n-octane from oil spills (19%). The remaining contributors mainly consist of zinc (11%) and fluoranthene (2%) from waste water.

Table 3.10 Normalization references for ETWA for Europe

Acute ecotoxicity in aquatic ecosystems	IP (ETWA) ¹ (m³/yr)	Population 2004 ²	Normalization references (m³/capita/year)
Albania	1.45E+07	3.13E+06	4.62E+00
Austria	5.76E+08	8.14E+06	7.08E+01
Belarus	4.53E+07	9.83E+06	4.61E+00
Belgium	7.08E+08	1.04E+07	6.81E+01
Bosnia/Herzegovina	1.82E+07	3.84E+06	4.74E+00
Bulgaria	4.85E+07	7.80E+06	6.22E+00
Croatia	6.98E+07	4.44E+06	1.57E+01
Czech Republic	2.12E+08	1.02E+07	2.08E+01
Denmark	9.08E+08	5.40E+06	1.68E+02
Estonia	1.83E+08	1.35E+06	1.36E+02
Finland	1.65E+09	5.22E+06	3.17E+02
France	1.25E+09	6.23E+07	2.00E+01
Germany	1.84E+09	8.25E+07	2.23E+01
Greece	4.34E+08	1.10E+07	3.93E+01
Hungary	2.00E+08	1.01E+07	1.98E+01
Ireland	6.60E+08	4.03E+06	1.64E+02
Italy	3.46E+09	5.79E+07	5.98E+01
Kalingrad region			
Kola Karelia			
Latvia	3.46E+08	2.32E+06	1.49E+02
Lithuania	2.20E+08	3.45E+06	6.39E+01
Luxembourg	6.58E+07	4.55E+05	1.45E+02
Moldova	5.09E+06	3.60E+06	1.41E+00
Netherlands	2.02E+09	1.63E+07	1.24E+02
Norway	2.02E+09	4.58E+06	4.40E+02
Poland	1.01E+09	3.82E+07	2.63E+01
Portugal	1.35E+08	1.05E+07	1.29E+01
Remaining Russia	2.43E+09	1.45E+08	1.67E+01
Romania	1.48E+08	2.17E+07	6.83E+00
Slovakia	8.23E+07	5.38E+06	1.53E+01
Slovenia	6.40E+07	2.00E+06	3.21E+01
Spain	1.84E+09	4.23E+07	4.34E+01
St-Petersburg			
Sweden	2.10E+09	8.98E+06	2.34E+02
Switzerland	7.02E+08	7.36E+06	9.54E+01
Ukraine	1.27E+08	4.73E+07	2.69E+00
United Kingdom	3.62E+09	5.97E+07	6.07E+01
Yugoslavia	1.05E+07	2.03E+06	5.17E+00
Europe ¹	6.69E+10	7.19E+08	9.30E+01

¹ Due to low data availability, the assessments of oil and TBT are not allocated among the concerned countries. Therefore, only the whole Europe impact potential includes those two categories.

² EUROSTAT-database (year 2004)

3.5.4.2 Chronic ecotoxicity in freshwater ecosystems (ETFWC)

Table 3.11 shows the substances that contribute to the normalization references (i.e. impact potentials) for ETFWC. The values for the normalization references are shown in Table 3.12.

Table 3.11 Substances contributing with 0.2% or more to the total impact potential (IP) for ETFWC

Substances	Fraction of IP
Lambda-cyhalothrin (pesticides)	38.7%
Betacyfluthrin (pesticides)	13.5%
Tau-fluvalinate (pesticides)	10.6%
Fluoranthene (via waste water)	8.3%
Cu (via waste water)	4.0%
Pb (via waste water)	3.6%
Hg (via waste water)	2.9%
Alpha-cypermethrin (pesticides)	2.6%
Cypermethrin (pesticides)	2.3%
HCB (airborne)	1.7%
Zn (via waste water)	1.5%
Benz(a)pyrene (via waste water)	1.4%
Cyfluthrin (pesticides)	1.3%
Pendimethalin (pesticides)	1.1%
Cu (airborne)	1.0%
PAHeq (airborne)	0.9%
Diflubenzuron (pesticides)	0.9%
Fluazinam (pesticides)	0.7%
Permethrin (pesticides)	0.5%
Cd (via waste water)	0.4%
Aclonifen (pesticides)	0.3%
Terbutylazin (pesticides)	0.2%
Mancozeb (pesticides)	0.2%
Zn (airborne)	0.2%
<i>Total</i>	98.3%

Chronic ecotoxicity in freshwater environment is largely dominated by pesticides (in total about 74% of the IP), particularly lambda-cyhalothrin (39%), betacyfluthrin (13%), and tau-fluvalinate (11%) are contributing. Fluoranthene is the most contributing “non-pesticide” accounting for 8.3%, whereas copper, lead and mercury emitted via waste water only contributes with 4.0%, 3.6% and 2.9% to the normalization reference for this impact category, respectively (see Table 3.11).

Table 3.12 Normalization references for ETFWC for Europe

Chronic ecotoxicity in freshwater ecosystems	IP (ETFWC) (m³/yr)	Population 2004 ¹	Normalization references (m³/capita/year)
Albania	5.99E+06	3.13E+06	1.92E+00
Austria	9.12E+06	8.14E+06	1.12E+00
Belarus	1.06E+06	9.83E+06	1.08E-01
Belgium	1.39E+07	1.04E+07	1.33E+00
Bosnia/Herzegovina	4.80E+05	3.84E+06	1.25E-01
Bulgaria	2.07E+07	7.80E+06	2.65E+00
Croatia	7.19E+06	4.44E+06	1.62E+00
Czech Republic	7.88E+06	1.02E+07	7.72E-01
Denmark	9.82E+06	5.40E+06	1.82E+00
Estonia	6.10E+06	1.35E+06	4.52E+00
Finland	9.15E+06	5.22E+06	1.75E+00
France	8.75E+07	6.23E+07	1.40E+00
Germany	7.03E+07	8.25E+07	8.51E-01
Greece	3.30E+07	1.10E+07	2.99E+00
Hungary	1.41E+07	1.01E+07	1.40E+00
Ireland	1.53E+07	4.03E+06	3.81E+00
Italy	1.03E+08	5.79E+07	1.78E+00
Kalingrad region			
Kola Karelia			
Latvia	2.10E+06	2.32E+06	9.06E-01
Lithuania	3.12E+06	3.45E+06	9.06E-01
Luxembourg	8.14E+05	4.55E+05	1.79E+00
Moldova	2.27E+07	3.60E+06	6.29E+00
Netherlands	2.61E+07	1.63E+07	1.61E+00
Norway	1.08E+07	4.58E+06	2.36E+00
Poland	2.41E+07	3.82E+07	6.32E-01
Portugal	9.80E+06	1.05E+07	9.35E-01
Remaining Russia	1.02E+08	1.45E+08	7.07E-01
Romania	4.69E+07	2.17E+07	2.16E+00
Slovakia	4.04E+06	5.38E+06	7.52E-01
Slovenia	1.85E+06	2.00E+06	9.29E-01
Spain	1.27E+08	4.23E+07	2.99E+00
St-Petersburg			
Sweden	1.26E+07	8.98E+06	1.40E+00
Switzerland	1.32E+07	7.36E+06	1.79E+00
Ukraine	5.71E+08	4.73E+07	1.21E+01
United Kingdom	6.03E+07	5.97E+07	1.01E+00
Yugoslavia	4.34E+06	2.03E+06	2.13E+00
Europe	1.46E+09	7.19E+08	2.03E+00

¹ EUROSTAT –database (year 2004)

3.5.4.3 Chronic ecotoxicity in marine ecosystems (ETMWC)

The contributing substances to the ETMWC impact potentials (IP) are presented in Table 3.13 and the values for the normalization references in Table 3.14.

Table 3.13 Substances contributing with 0.1% or more to the total impact potential (IP) for ETMWC

Substances	Fraction of IP
Cu (via waste water)	32.4%
Hexachlorobenzene (airborne)	15.0%
Zn (via waste water)	12.3%
Cu (airborne)	8.8%
Fluoranthene (via waste water)	8.0%
PAHeq (airborne)	7.7%
TBT	3.4%
n-octane	2.1%
Pb (via waste water)	2.0%
Zn (airborne)	1.8%
Hg (via waste water)	1.6%
Pb (airborne)	1.2%
Benz(a)pyrene (via waste water)	1.2%
Hg (airborne)	0.9%
Ni (airborne)	0.5%
Hexachlorobenzene (via waste water)	0.4%
Cd (airborne)	0.1%
Cd (via waste water)	0.1%
<i>Total</i>	99.7%

As shown in Table 3.13 copper plays a dominant role for the impact potential, with a contribution of 41% (both air-borne and from waste water), along with hexachlorobenzene, HCB (15%) and zinc 14% (both air-borne and from waste water). The remaining part is split into several compounds, such as fluoranthene via waste water (8%), PAHs from atmospheric depositions (7.7%) and tributyltin (3.4%).

Table 3.14 Normalization references for ETMWC for Europe

Chronic ecotoxicity in marine ecosystems	IP (ETMWC) ¹ (m ³ /yr)	Population 2004 ²	Normalization references (m ³ /capita/year)
Albania	1.77E+06	3.13E+06	5.67E-01
Austria	1.98E+07	8.14E+06	2.43E+00
Belarus	5.76E+06	9.83E+06	5.87E-01
Belgium	2.78E+07	1.04E+07	2.68E+00
Bosnia/Herzegovina	2.75E+06	3.84E+06	7.17E-01
Bulgaria	6.10E+06	7.80E+06	7.82E-01
Croatia	3.07E+06	4.44E+06	6.90E-01
Czech Republic	9.23E+06	1.02E+07	9.04E-01
Denmark	1.73E+07	5.40E+06	3.20E+00
Estonia	7.70E+06	1.35E+06	5.70E+00
Finland	4.42E+07	5.22E+06	8.46E+00
France	5.29E+07	6.23E+07	8.50E-01
Germany	1.38E+08	8.25E+07	1.67E+00
Greece	2.11E+07	1.10E+07	1.91E+00
Hungary	8.58E+06	1.01E+07	8.48E-01
Ireland	2.15E+07	4.03E+06	5.34E+00
Italy	1.12E+08	5.79E+07	1.94E+00
Kalingrad region			
Kola Karelia			
Latvia	1.09E+07	2.32E+06	4.72E+00
Lithuania	8.99E+06	3.45E+06	2.61E+00
Luxembourg	2.28E+06	4.55E+05	5.01E+00
Moldova	6.27E+05	3.60E+06	1.74E-01
Netherlands	6.87E+07	1.63E+07	4.23E+00
Norway	5.10E+07	4.58E+06	1.11E+01
Poland	4.45E+07	3.82E+07	1.17E+00
Portugal	8.72E+06	1.05E+07	8.32E-01
Remaining Russia	1.67E+08	1.45E+08	1.15E+00
Romania	1.07E+07	2.17E+07	4.93E-01
Slovakia	5.45E+06	5.38E+06	1.01E+00
Slovenia	2.97E+06	2.00E+06	1.49E+00
Spain	1.49E+08	4.23E+07	3.51E+00
St-Petersburg			
Sweden	5.54E+07	8.98E+06	6.17E+00
Switzerland	2.34E+07	7.36E+06	3.18E+00
Ukraine	4.94E+07	4.73E+07	1.05E+00
United Kingdom	1.20E+08	5.97E+07	2.00E+00
Yugoslavia	1.45E+06	2.03E+06	7.15E-01
Europe ¹	1.36E+09	7.19E+08	1.89E+00

¹ Due to low data availability, the assessments of oil and TBT are not allocated among the concerned countries. Therefore, only the whole Europe impact potential includes those categories.

² EUROSTAT-database (year 2004)

3.5.4.4 Chronic ecotoxicity in terrestrial ecosystems (ETSC)

The substances contributing to the normalization references (i.e. impact potentials) for ETSC are presented in Table 3.15 and the values for the normalization references in Table 3.16.

Table 3.15 Substances contributing with 0.1% or more to the total impact potential (IP) for ETSC

Substances	Fraction of IP
Lambda-cyhalothrin (pesticides)	44,5%
Betacyfluthrin (pesticides)	15,9%
Tau-fluvalinate (pesticides)	12,5%
Cypermethrin (pesticides)	6,9%
PAHeq (airborne)	4,4%
Alpha-cypermethrin (pesticides)	2,8%
Fluazinam (pesticides)	2,0%
Cu (airborne)	2,0%
Cyfluthrin (pesticides)	1,6%
Pendimethalin (pesticides)	1,1%
Diflubenzuron (pesticides)	0,9%
HCB (airborne)	0,9%
Aclonifen (pesticides)	0,5%
Tebuconazole (pesticides)	0,4%
Prosulfocarb (pesticides)	0,4%
Zn (airborne)	0,4%
Azoxystrobin (pesticides)	0,3%
Esfenvalerate (pesticides)	0,3%
Pb (airborne)	0,3%
Terbuthylazin (pesticides)	0,2%
Cu (sewage sludge to agriculture)	0,2%
Hg (airborne)	0,2%
Ni (airborne)	0,1%
Total	98,7%

Pesticides largely dominate the normalization reference for the impact category on *ecotoxicity in terrestrial ecosystems* with a major contribution from lambda-cyhalothrin (44%), betacyfluthrin (16%), tau-fluvalinate (12%) and cypermethrin (7%). Atmospheric depositions of PAH (4%) and metals (copper: 2%), along with several other pesticides complete the distribution.

Table 3.16 Normalization references for ETSC for Europe

Chronic ecotoxicity in terrestrial ecosystems	IP (ETSC) ¹ (m³/yr)	Population 2004 ²	Normalization references (m³/capita/year)
Albania	3.59E+08	3.13E+06	1.15E+02
Austria	1.74E+08	8.14E+06	2.14E+01
Belarus	1.00E+08	9.83E+06	1.02E+01
Belgium	4.91E+08	1.04E+07	4.72E+01
Bosnia/Herzegovina	4.30E+07	3.84E+06	1.12E+01
Bulgaria	1.25E+09	7.80E+06	1.61E+02
Croatia	3.86E+08	4.44E+06	8.70E+01
Czech Republic	3.61E+08	1.02E+07	3.54E+01
Denmark	3.38E+08	5.40E+06	6.27E+01
Estonia	4.37E+07	1.35E+06	3.24E+01
Finland	1.10E+08	5.22E+06	2.11E+01
France	3.46E+09	6.23E+07	5.56E+01
Germany	2.25E+09	8.25E+07	2.73E+01
Greece	1.73E+09	1.10E+07	1.56E+02
Hungary	7.26E+08	1.01E+07	7.17E+01
Ireland	5.33E+07	4.03E+06	1.32E+01
Italy	4.04E+09	5.79E+07	6.98E+01
Kalingrad region			
Kola Karelia			
Latvia	8.35E+07	2.32E+06	3.60E+01
Lithuania	6.44E+07	3.45E+06	1.87E+01
Luxembourg	8.03E+06	4.55E+05	1.77E+01
Moldova	1.34E+09	3.60E+06	3.72E+02
Netherlands	7.20E+08	1.63E+07	4.43E+01
Norway	5.49E+07	4.58E+06	1.20E+01
Poland	1.22E+09	3.82E+07	3.19E+01
Portugal	4.52E+08	1.05E+07	4.31E+01
Remaining Russia	4.57E+09	1.45E+08	3.15E+01
Romania	2.75E+09	2.17E+07	1.27E+02
Slovakia	2.13E+08	5.38E+06	3.96E+01
Slovenia	8.43E+07	2.00E+06	4.22E+01
Spain	5.65E+09	4.23E+07	1.33E+02
St-Petersburg			
Sweden	1.24E+08	8.98E+06	1.39E+01
Switzerland	3.21E+08	7.36E+06	4.36E+01
Ukraine	3.40E+10	4.73E+07	7.18E+02
United Kingdom	1.07E+09	5.97E+07	1.80E+01
Yugoslavia	2.58E+08	2.03E+06	1.27E+02
Europe	6.89E+10	7.19E+08	9.58E+01

¹ Discrepancies occur among countries in the way of assessing pesticide use. Overall, pesticides are assessed using sales, which might differ from consumptions, and their inventories rely on the Danish use.

² EUROSTAT-database (year 2004)

3.5.5 Discussion

3.5.5.1 Acute ecotoxicity in the aquatic environment

National assessments

Among the assessed countries, the northern Europe ones are characterized by the highest normalization references. The national normalization references do not include the assessment of oil and tributyltin (TBT), and therefore the dominating substances are heavy metals via waste water. It must be pointed out that these northern countries are those for which data are the best reported and probably the most comprehensive. For other countries, it is likely that monitoring is not entirely reliable and a look at the type of data referring to each country (not shown here) testifies that a large part of southern countries were assessed using extrapolations. Thus, underestimations are likely to occur for most of southern and central European countries.

Taking this into account and because oil spills and TBT are not included in the national assessments, it is recommended to use the normalization reference for the whole Europe (total).

Normalization reference for Europe

The impact potential for Europe is equally split between TBT, which exerts a very high toxicity towards aquatic organisms, and heavy metals via waste water, both accounting for ca. 40%, while oil spills add up to about a 100%. Overall, this contribution is consistent with the one obtained by Stranddorf et al. (2005b), who reported contributions from TBT and heavy metals via waste water of 50% and about 40%, respectively, see Table 3.17.

Table 3.17 Distribution of the impact potentials for EDIP97 and EDIP 200X for acute ecotoxicity in the aquatic environment

IP% (ETWA)	EDIP200X ¹ This study	EDIP97 ² Stranddorf et al. (2005b)
Heavy metals via waste water	40.9%	38.7%
Organic substances via waste water	2.3%	10.7%
Oil discharges	19.4%	0.7%
TBT	37.4%	49.9%

¹ Distributions for Europe as a whole (35 countries)

² Distributions for EU-15

The main difference between the two sets of contributions is associated with the category 'oil discharges', which was evaluated under different approaches in the two cases. In Stranddorf et al. (2005b), oil compounds were evaluated as a whole with one single characterization factor, while in the present study, a differentiation was attempted to assess each chemical individually. Hence the fact that oil-related n-octane appears to be highly contributing here (Table 3.9) and not in the EDIP97 assessment by Stranddorf et al. (2005b), is reflected in Table 3.17.

However, it must be stressed that the contribution of oil spills occurring mainly in marine environment might be underestimated (also for chronic ecotoxicity). This is because only 32% of the discharges are assessed (depending on the availability of characterization factors) and those discharges are mainly limited to the North Sea. In addition, the fact that discharges were extrapolated from an incomplete speciation (the original average speciation includes only 27% of the average crude oil composition; see Appendix V) might reinforce this probable underestimation, i.e. several oil-related compounds may not be covered. Finally, it must also be pointed out that the used specification (shown in Appendix V) is an average

based on a number of studies and it is known that the composition of oil largely differ depending on parameters such as the extraction location (Fingas and Fieldhouse 2004).

Further it must be stressed that the EDIP97 and EDIP200X methodologies are quite different. One of the main differences is that EDIP97 is based on no-effect values (i.e. PNECs) whereas EDIP200X is based on effect values (i.e. EC50 based HC50s), see Section 3.1 and 3.2 for details.

Nota: Table V-2 in Appendix V clearly shows that the used percentage for n-octane (2.87%) outnumbers the maximum one reported by the TPH CWG (Potter and Simmons 1998), i.e. 1.90%, meaning that it is likely that, with respect to emission data, n-octane was overestimated in the present assessment (factor ca. 1.5).

3.5.5.2 Chronic ecotoxicity in freshwater ecosystems

Overall, pesticides largely dominate the normalization reference for ETFWC, with a contribution of 74% to the total impact potential (see Table 3.11). This is the result of emissions of particularly potent active ingredients, such as lambda-cyhalothrin and betacyfluthrin, to air. The contribution from pesticides is about equally distributed among emissions via air and emissions via run-off (and drainage), i.e. 58% and 42%, respectively. However, these emissions rely on extrapolations from the consumptions in Denmark. Agriculture modes are expected to vary a lot from one country to another, and therefore the apportionment in active ingredients might differ significantly. Besides, the list of active ingredients used in Denmark is probably not fully valid for other countries, for which different regulations might be in force.

Among the remaining 26% of the impact potential, heavy metals and organic substances via waste water mainly dominate, particularly fluoranthene, copper, lead and mercury. However, large approximations were done when quantifying releases of heavy metals. Indeed, as already pointed out in the methodology part, most of emissions of heavy metals are reported as inputs to the seas. That implies that the used figures rely on the modeling to estimate direct emissions to freshwater, i.e. the first-order removal equation assuming an average time of 40 days for the substances to reach the coasts (cf. Section 3.1.2.3). Furthermore, as the used emission data mainly cover northern countries extrapolations were performed to assess most of southern and central European countries.

Regarding fluoranthene, and all other organic compounds reaching the freshwater environment via waste water, it must be stressed that the emission data rely on extrapolations from a study focusing on the Netherlands in 1994 (Van der Auweraert et al. 1996). Consequently, large uncertainties are associated with these emission data. When focusing on poly-aromatic hydrocarbons (PAH), other sources report a lower emissions than the ones used in the present study. According to the European Pollutant Emission Register (EPER), the emissions of PAH to water in the EU only reached 27 tons in 2001 (EC 2005). Nevertheless, it must be stressed that, at the time of writing, the EPER cannot be considered fully comprehensive (cross-checking with other regularly updated data sources, such as EMEP/CEIP-database or OSPAR). Another source states that 98 tons PAH per year ended up in the water environment in Europe beginning of the 2000s (SOCOPSE 2008). Both of these sources are draft reports.

Regarding yearly releases to freshwater in the present study the data from Van der Auweraert (1996) were extrapolated to get amounts of 65.1 tons and 308 tons of benzo[a]pyrene and fluoranthene, respectively (these two compounds are the main representatives of the PAH in the current inventory). Even though these figures are covering 35 European countries, and not only the EU countries, they might be overestimated.

With respect to other assessments dealing with normalization references for chronic freshwater ecotoxicity Wegener Sleeswijk et al. (2008) report a distribution focused on chlorine (ca. 70%) and pesticides (ca. 25%) as main contributors. They state that whether or not chlorine is a significant contributor still is in need of research. In the present study, chlorine was not included in the inventory due to lack of consistent data. However, disregarding chlorine, it can be seen that pesticides turn out to dominate the impact category in both Wegener Sleeswijk et al. (2008) and the present assessment.

Sensitivity analysis

As mentioned in Section 3.5.3.6 the study by Birkved and Hauschild (2006) and Linders et al. (1994) indicates that as much as 1% of the total pesticide active ingredient (a.i.) consumption may end up in freshwater via run-off and drainage. A sensitivity analysis was therefore performed making the pesticide emissions (run-off and drainage) to reach the freshwater environment account for 1% of the total active ingredient consumptions instead of 0.1% as used in the main assessment (cf. Section 3.5.4.2). Results are presented in Table 3.18.

Table 3.18 Sensitivity analysis on the normalization reference for ETFWC, assuming a run-off/drainage accounting for 1% of the total pesticide (a.i.) emissions instead of 0.1% as used in the main assessment

IP% (ETFWC)	Main assessment (run-off: 0.1% of total emissions)	After sensitivity analysis (run-off: 1% of total emissions)
Heavy metals (via waste water)	12.4%	3.3%
Organic substances (via waste water)	9.7%	2.5%
Atmospheric depositions ¹	4.0%	1.1%
Pesticides ²	73.9%	93.1%
Normalization references (m³/cap/yr)	2.03E+00	7.70E+00

¹ Atmospheric depositions consist of air emissions of heavy metals, and a few organic substances, which deposit on freshwater.

² Pesticides consist of emissions of active ingredients to freshwater ecosystems from run-off/drainage and air-borne releases, which deposit afterwards.

If a run-off/drainage percentage of 1 is used the normalization reference for ETFWC is increased by approximately a factor 4, while the role played by pesticides in the overall picture becomes largely predominant (93% of the total impact potential instead of 74%), see Table 3.18. The contribution from pesticides is now divided into 81.9% from run-off/drainage and the rest, i.e. 11.2%, from air emissions redistributed to freshwater.

This sensitivity analysis demonstrates the significance of the pesticides to characterize ecotoxicity in freshwater ecosystems, and particularly the part which ends up in rivers/lakes due to run-off and drainage.

3.5.5.3 Chronic ecotoxicity in marine ecosystems

National assessments

The countries with the highest normalization references for ETMWC turned out to be approximately the same as for ETWA, i.e. the Nordic countries, Ireland, Benelux and Spain (Table 3.12 and 3.14). The impact potentials for those countries are mainly driven by heavy metals via waste water and by atmospheric depositions (for Spain, this last category is highly dominant). As already highlighted, emission data for water-borne emissions of heavy metals suffer from a lack of completeness and, though they are considered the best available reported data at the time of writing, they are likely not to be entirely representative of the actual situation.

For those reasons, added to the fact that oil and TBT are not regarded in the national assessments, it is recommended to use the normalization reference for Europe (total).

Comparisons with other assessments

Emissions of heavy metals via waste water (and air) highly contribute (in total about 62%) to the total impacts in ETMWC with copper (32%) and zinc (12%) as main contributing substances, see Table 3.13. When comparing to the distribution in ETWA (Table 3.9), tributyltin (TBT) is no more significant in the global picture, which may be due to the fate data used to estimate is characterization factor for ETMWC (see sensitivity analysis below). Similarly, n-octane is also characterized by a relatively little contribution to the impact potential (2%) as compared to ETWA (19%).

Those points can be compared with the study by Wegener Sleeswijk et al. (2008), who obtained a normalization reference regarding “marine ecotoxicity” (chronic effects) apparently without any significant contribution from TBT and n-octane (though no evidence that n-octane was included in Wegener Sleeswijk study was found). Moreover, in the present assessment, copper plays a significant role (32%, aggregating air-borne and water-borne emissions), which is also attested by Wegener Sleeswijk et al. (2008) reporting a contribution of 16% for copper, EU-25+3 (though the input data used by Wegener Sleeswijk et al. are not exactly known and are likely to differ from those used in the present study).

When comparing with the EDIP97 normalization references (Stranddorf et al. 2005b), it turns out that major discrepancies occur regarding TBT and atmospheric depositions (see Table 3.19). While TBT accounts for more than 40% in EDIP97, its contribution is much smaller in EDIP200X (3.5%). The explanation is likely to result at least partly from differences in the fate modeling of the two methods being more comprehensive in EDIP200X. Regarding the atmospheric depositions, the explanation for the high difference (36.2% as compared to 9.5%) comes from the fact that emissions of organic substances, such as hexachlorobenzene (HCB) or poly-aromatic hydrocarbons (PAH) to air, is not included in the inventory by Stranddorf et al. (2005b). The fact that these two substances (HCB and PAH) represent almost 23% (Table 3.13) of the total ETMWC impact potential for the EDIP200X, clearly support this statement.

Table 3.19 Distribution of the impact potentials for EDIP97 and EDIP200X for chronic marine ecotoxicity

IP% (ETMWC)	EDIP 200X ¹ This study	EDIP 1997 ² Stranddorf et al. (2005b)
Heavy metals (via waste water)	48.4%	32.0%
Organic substances (via waste water)	9.6%	14.5%
Oil discharges	2.3%	2.7%
TBT	3.45%	41.4%
Atmospheric depositions ³	36.2%	9.5%

¹ Distribution for Europe as a whole (35 countries) for chronic marine ecotoxicity

² Distribution for EU-15 for chronic ecotoxicity in aquatic environment (most of the emission data used in Stranddorf et al. (2005b) are related to inputs to marine environment)

³ Atmospheric depositions consist of air emissions of heavy metals, and a few organic substances, which deposit on marine environment

Sensitivity analysis

Due to the possible large impact of tributyltin (TBT) on the result and high variability in available fate data, a sensitivity analysis was performed on this particular compound. It only

focuses on the characterization factor though it should be kept in mind that emission data are also likely to be a source of potentially large variations. Two variations were considered here and the results are shown in Table 3.20:

- The value of the characterization factor for TBTF (tributyltin fluoride) used in the main assessment relies on a half-life in water environment of 8.6 days (from the USETox database: Rosenbaum et al. 2008) which is consistent with Seligman et al. (1988, 1989), who reported a half-life ranging between 4 and 19 days in seawater. However, since dibutyltin (DBT) is the overall dominating metabolite and also relatively toxic (ECOTOX 2009) and since the mineralization half-life of TBT is about 40 days (Seligman et al. 1988), a half-life of 40 days was used in the sensitivity analysis.
- Apparently no definite Henry's law constant (H) exist for compounds related to tributyltin and different data sources give different values (PhysProp 2009, EPI Suite 2009, USETox database: Rosenbaum et al. 2008). In the main scenario here a characterization factor for TBTF of $4.49\text{E}+2 \text{ m}^3/\text{kg}$ is used. This factor is based on a Henry's law constant (H) of $1.3\text{E}+4 \text{ Pa}\cdot\text{m}^3/\text{mol}$ (USETox database: Rosenbaum et al. 2008) indicating that a high proportion of TBT will evaporate from water. As more realistic alternatives to be used in the modeling an H value of $2.4\text{E}-2 \text{ Pa}\cdot\text{m}^3/\text{mol}$ (estimated on basis water solubility and vapor pressure from PhysProp 2009) or $2.6\text{E}-3 \text{ Pa}\cdot\text{m}^3/\text{mol}$ (EPI Suite 2009) may be used. These alternative figures indicates that a high proportion of TBT will stay in water which is probably more realistic as TBT (i.e. TBT-oxide) to a high degree will adsorb to suspended matter in water (INCHEM 2009). Using these alternative H value leads to a characterization factor of $1.16\text{E}+4 \text{ m}^3/\text{kg}$ in both cases.

Table 3.20 Sensitivity analysis on the normalization reference for ETMWC, assuming a half-life of 40 days and two alternative Henry's law constants (H) for TBT

<i>IP% (ETMWC)</i>	<i>Main assessment Half-life=8.6 days H=13,000 Pa·m³/mol</i>	<i>After sensitivity analysis (half-life of 40 days)</i>	<i>After sensitivity analysis (H = 0.0026 or 0.024 Pa·m³/mol)</i>
Heavy metals (via waste water)	48.4%	43.0%	17.6%
Organic substances (via waste water)	9.6%	8.6%	3.5%
Oil discharges	2.3%	2.0%	0.8%
TBT	3.45%	14.2%	64.8%
Atmospheric depositions ¹	36.2%	32.2%	13.2%
Normalization references (m³/cap/yr)	1.89	2.13	5.19

¹ Atmospheric deposition consists of air emissions of heavy metals, and a few organic substances, which deposit on marine environments.

These sensitivity analyses stress the uncertainties underlying with TBT characterization and its consequences on the normalization reference for ETMWC. Considering a half-life of 40 days increases the contribution of TBT to 14%, while changing the Henry's law constant makes it reach about 65%, increasing the normalization reference by a factor 2.7. So, even though this raises the need for definite datasets regarding TBT in order to improve the consistency of the whole impact assessment, the ETMWC normalization reference is only varying within a factor of about 3 depending on the data used.

3.5.5.4 Chronic ecotoxicity in terrestrial ecosystems

National assessments

Overall southern and central European countries are the most affected by terrestrial ecotoxicity. With respect to the distribution of the impact potentials (90% is due to pesticides), it is rather problematic since those countries are the ones for which no consistent data about consumptions of pesticides were obtained. Therefore, most of those countries are characterized using their sales of pesticides, which might not correspond to their actual consumptions (due to e.g. stocks, import/exports). Though the right order of magnitude is expected in the final results, large uncertainties still remain.

Thus, national assessments could be used as a first step for sensitivity analysis or for future work about spatial differentiation as tendencies in emission data are depicted in the present study. However, uncertainties, associated with those emission data depending on which country is in focus, would lead to a lack of representativeness in the normalization references for some countries (particularly in southern and central Europe). For that reason, only the normalization reference for Europe (total) is recommended for use.

Comparisons with other assessments

Pesticides turn out to be largely dominant in the impact assessment (>90% of the total impact potential), with a distribution very similar to the one obtained for ecotoxicity in freshwater ecosystems (ETFWC). It can be pointed out that this pesticide contribution is almost entirely resulting from emissions of active ingredients to air (due to wind drift and volatilization), which deposit on the terrestrial and aquatic ecosystems afterwards. This domination of pesticides is confirmed by other assessments: Wegener Sleeswijk et al. (2008), who considered the emission year 2000, reported a total contribution of 60% for pesticides, while Stranddorf et al. (2005b), who covered the emission year 1994, found a contribution of ca. 100% to the total impact potential for ecotoxicity in terrestrial ecosystems (in the latter case, no specification of active ingredients was performed).

However, it must be noted that the assessment from Wegener Sleeswijk et al. (2008) and the one from the present study are likely to differ largely in their inventories because no consistent data about the consumptions of pesticide active ingredients at the full European scale are yet available today. In the present report, extrapolations to Europe were performed based on active ingredient consumptions in Denmark. It introduces uncertainties because European countries show different ways of cultivating land and most probably do not use exactly the same pesticides as in Denmark. Thus, discrepancies in the obtained contributions are more likely to result from differences in the input data and the used methodology than from actual variation in the normalization references. It clearly emphasizes the need for more comprehensive data to assess this impact category.

3.5.5.5 Uncertainties and bias

Uncertainties

This section mainly deals with uncertainties related to emission data, as overall methodological uncertainties is outside the scope of this study:

- TBT: In this study, the original source refers to release estimates of TBT in the marine environment from Denmark (DEPA 1997). Apart from the fact that emission data rely on estimates, the extrapolation performed using marine areas might turn out to be very rough and therefore, large uncertainties in the obtained assessment of TBT are expected. Those uncertainties may have an impact on the normalization reference for ETWA, as TBT is by far the most contributing substance in this impact, as well as for ETMWC. A large source of uncertainty is also underlying the characterization factors for TBT, which are dependent on its properties. The fact that those properties are not

set in an unequivocal way (even though this is actually also the case for many other substances) becomes especially problematic in this case as TBT is essential for the normalization references as shown in Table 3.20.

- Oil compounds: n-Octane turned out to be quite relevant in this study. As its emission data hinge on an average crude oil specification (cf. Appendix IV), that contribution must be handled with care and actual releases of this compound should be better investigated. The main potential consequences of those uncertainties are related to the normalization reference for ETWA (n-octane accounts for about 19%, Table 3.9).
- Heavy metals: It is very likely that heavy metals discharges (mainly via waste water and air-borne emissions for some of them) are underestimated in this study, as large discrepancies occur in the way of reporting them among the assessed countries. Overall, northern countries can be credited with a good representativeness, while southern and central European countries are characterized by a prominent lack of reliable data (extrapolations were used to address this lack of data). As heavy metals are relevant in all four impacts (particularly for copper and to a lesser degree zinc), those uncertainties might induce significant impacts on all four impact normalization references.
- Organics (via waste water): Data on organics at a European scale entirely rely on extrapolations from a study conducted in the Netherlands in 1996. Two main sources of uncertainties can be identified: the out-of-date aspect of the original emission figures for the Netherlands and the potential miscorrelation between the releases of organics and the Gross Domestic Products used in the extrapolations. Those uncertainties might have an impact on the normalization references for all impacts related to ecotoxicity in the aquatic ecosystems.

Nota: Uncertainties are also associated for discharges via waste water (organic substances but also heavy metals) when performing the clear cut between direct emissions to freshwater and inputs to marine environments. The first-order degradation/removal as well as the time of 40 days to reach the seas (both taken from the modeling in EDIP200X) might be subject to discrepancies with the actual situations.

- Pesticides: As already pointed out, emission data rely on extrapolations of active ingredient consumptions in Denmark. Therefore, large uncertainties are expected for the obtained figures for Europe, as agriculture habits differ from one country to another. The comprehensiveness of the list of active ingredients as well as the consumptions themselves of these compounds at a European level might be questionable. However, it is difficult to estimate the impact of those uncertainties on the final results though it is very likely to induce significant changes as pesticides account for 75% and 90% to the total impact potentials for freshwater ecotoxicity and terrestrial ecotoxicity, respectively.

Bias

As stated by Heijungs et al. (2007), apart from uncertainties, bias might occur in the normalization references, and induce inconsistent results when conducting an LCA study. Such a case happens when the LCA study implies a significant role from peculiar compounds and these compounds are not part of the normalization reference (i.e. normalization inventory). The normalization references then become unrepresentative and the obtained result after such normalization is biased.

Although no quantification has been done, this situation may be relevant in the present study. Indeed, the EDIP200X database includes characterization factors for over 2 000 compounds. Obviously, not all of them could be assessed as many are not monitored. Therefore, a great care must be considered when handling cases with peculiar processes (e.g. chemical processes) and it is recommended first to check the consistency with the normalization references (inclusion of proper emission data).

This issue is further investigated in Chapter 10 as related to EDIP97-methodology and the NEPTUNE relevant case of including “new” substances, i.e. pharmaceuticals.

3.5.6 Conclusions and recommendations

This study was conducted in order to provide a first proxy of the normalization references for the recently developed EDIP 200X ecotoxicity methodology. The geographical scope was set to Europe as a whole, though a differentiation in emission data among the assessed countries was performed. That differentiation can be the basis for sensitivity analysis or for side works. Furthermore, large discrepancies in the data availability among the different countries were observed. A huge effort is thus needed for some countries to report and provide reliable and consistent emission data, which remains, at the moment, the main weakness in the settings of the normalization references.

In the context of LCA and considering the amount of available characterization factors, it is also recommended to check the input data of the case and test their correlation with the emission data used to set the normalization references. That last point is to be put into perspective as results showed that only a few substances are responsible for the largest parts of the impact potentials. That the (few) significant contributing substances are included in the normalization references therefore becomes critical.

Finally, beside the recommendation to update normalization references as soon as consistent emission data are readily available, it could also be useful to extend the geographical scope to the whole world, i.e. to set normalization references for Asia or North America. Indeed, when dealing with globalized processes, Life Cycle Assessments should require normalization references differentiated for each specific economic system (e.g. North America), and not only Europe. Obviously, it implies a need for consistent emission data for each defined economic system. With respect to growing globalization, this stage is to become necessary in the perspective of management of global environmental sustainability.

4 Substances with specific toxic mode of action

The main part of the substances included in LCIA ecotoxicity characterization until now is substances with a narcotic toxic mode of action (i.e. non-specific) and/or substances for which it is assumed that this is the mode of action. The impact assessment methodology is therefore (as in most generic risk assessment) addressed at narcotics and in many cases based on (measured) acute values extrapolated to chronic values by use of application factors, AF (typically 10-1000). However, substances like endocrine disrupters and pharmaceuticals have specific toxic mode of action (TMoA) and using an acute value multiplied by an AF in order to reach a PNEC value (or chronic GMtroph) will in many cases be quite misleading as some of these substances have a very low acute toxicity but very high chronic toxicity. For example ethynylestradiol (EE2) has an aquatic chronic PNEC value around 0.1 ng/L but its lowest acute toxicity is at the level 1 mg/L (Clauson-Kaas et al. 2006). So, in this case an AF of 10^7 would be needed which is totally out of proportion as compared to the typically recommended range (10-1000) and with no sense as the mechanism for acute toxicity is not at all related to the mechanism of the chronic toxicity. Taking this example as a case and using the recommended procedure from the EDIP97 methodology (Hauschild et al. 1998b) we will end up underestimating the chronic PNEC value by a factor of 10,000.

So, using chronic values and knowing the TMoA (or at least the most sensitive end point) is very important for many of the “new” substances included in the NEPTUNE project. A way to address this is shown below for endocrine disrupters.

4.1 Endocrine disrupters

For endocrine disruptors (EDS) the TMoAs are many but they are all related to disturbance of the homeostasis of the endocrine system in living organism. An endocrine disrupter or sex hormone disrupter may be defined as “an exogenous substance that causes adverse health effects related to the reproductive function of an intact organism or its progeny, consequent to changes in endocrine function” (OECD 2001). Effects on the level of populations may be included in this definition (Vethark et al. 2006).

When dealing with ecotoxic effects within LCIA the choice of relevant endpoints and degree of standardization of the test set-up are very important due to the comparative framework of LCIA which calls for best estimates and not conservative values as may fit in tiered risk assessment. In order to have at least an indication of environmental relevance as regards impacts on the ecosystem (e.g. species diversity) population relevant endpoints are recommended. Standardized laboratory tests with endpoints like mortality, growth or reproduction are therefore preferred as opposed to avoidance tests or change in hepatic enzyme activity. Further details on this issue may be found in Larsen and Hauschild (2007b).

Looking at especially estrogens and the existing standardized laboratory tests, fish species are dominating because of a sensitive sex hormone system. Algae are not relevant in this case and tests on invertebrates (e.g. daphnia, copepods) are not at all developed to the degree of the fish tests.

The endpoints included in the fish tests on endocrine disruptions are all related to sex characteristics. Morphological changes like color and shape, biochemical markers like vitellogenin (VTG) induction and gonad histology are all included. In published results the induction of VTG and change in sex ratio of a population are dominating (OECD 2004).

VTG is a precursor of the egg yolk protein that normally occurs in sexually-active females. Its induction is controlled by the interaction between estrogens and the estrogen receptors in the

fish. It may be used as a biomarker for estrogenic compounds as well as anti-estrogenic compounds and androgens. However, there is still a need for research in order to understand the importance of an increase in VTG in biological terms (OECD 2004). So, we are here dealing with a biomarker whose relation to the reproduction of the fish (or fish population) is not fully clarified.

Change in sex ratio is per se a population relevant endpoint. It is typically identified by gonad histology of the tested fish population (OECD 2004, Jackson 2005). A 60-120 days exposure Fish Sexual Development Test (FSDT) is undergoing validation as an OECD test guideline (Holbech et al. 2008, Örn et al. 2003; Holbech et al. 2006) including several fish species (e.g. zebra fish and fathead minnow). As change in sex ratio apparently relates directly to the reproduction of a fish population this endpoint is considered more relevant than VTG when dealing with LCIA.

Based on existing knowledge, i.e. LCIA relevance and sensitivity of laboratory tests/endpoints, it is recommended to use test results from fish laboratory tests with the endpoint sex ratio as effect data when estimating ecotoxicity characterization factors for especially estrogenic compounds. VTG test results may only be used as secondary choice in case of no data on sex ratio. If a PNEC approach is used it is recommended to use an application factor of 10 on the lowest fish NOEC. However, it should be noticed that all these recommendations are preliminary as the area is still strongly progressing.

5 Whole effluent toxicity

As opposed to a single substance approach whole effluent toxicity (WET) is dealing with acute and /or chronic measurements on the whole effluent (i.e. the mixture). Its use is expanding within effluent quality assessment but primarily as a supplement to single substance based tests/assessments (ECETOC 2004).

Tests on whole effluent may include both tests on ecotoxicity effect and its persistence, and even assessments regarding bioaccumulation may be included. It may then be designated as whole effluent assessment (WEA). However, test on persistence of toxicity and bioaccumulation (actually of components not the whole mixture) is still under development. Regarding existing standard tests on persistency/biodegradation used in tests for persistency of toxicity (and bioaccumulating components) tests for inherent biodegradability may be the least inferior (ECETOC 2004). The problem is that a standard biodegradability test is not designed for mixtures but for single substances, so, test for readily biodegradability of a mixture is meaningless as this test guideline implicitly assumes that the possible remaining substance fraction after minimum 60% – 70% mineralization has the same degradation properties as the mineralised part.

In NEPTUNE no fate tests like tests on toxicity persistence are included. The WET tests included in the NEPTUNE testing program comprise yeast tests on (anti-) estrogenicity, (anti-) androgenicity and mutagenicity and results from these tests are used to assess cytotoxicity. Further, chronic tests on five European aquatic species (plant, invertebrates and vertebrate) and tests for pathogens (bacterial and viral indicators) are included (Lachmund et al. 2007). Besides the microbial tests, which are dealt with in chapter 6, these tests are dealt with at the end of this chapter.

When doing impact assessment in LCA we are integrating and comparing potential ecotoxic impacts appearing at different places in space and time. For example in NEPTUNE we are comparing the avoided impacts from treating the waste water with the induced impacts from building, running and decommissioning the treatment plant (Larsen et al. 2007).

The typical way of including potential ecotoxicity impact in LCIA is by use of characterization factors based on single substances, i.e. a substance orientated approach. As described in chapter 3 each substance is characterised by use of fate and effect modelling. There are several reasons for this of which the above mentioned LCIA characteristics on integration in time and space are among the most important. Demands and constraints on LCIA related to ecotoxicity are compiled in Larsen and Hauschild (2007a).

The single substance approach used in LCIA is implicitly assuming (concentration) additivity of toxicity (Payet 2004), whereas WET tests directly measure the mixture toxicity. Even though additivity might be the dominating phenomena in waste water (Pedersen et al. 1994) mixtures showing antagonistic and synergistic effects/endpoints might occur (Deneer 2000, Andersen et al. 2009) and waste water typically has a complex composition that is not fully known, and unknown compounds might contribute significantly to its toxicity.

If results from WET tests are to be included in LCIA of waste water treatment technologies (WWTTs) we are facing at least the following challenges:

- Unequal data availability resulting in possible bias of the LCA results
- Lack of fate data, i.e. persistence, distribution among environmental compartments

We do not know anything about the fate of the toxicity measured by WET in one cubic meter of waste water (i.e. the functional unit, fu) but it is most probably complex due to the content in the water of different substances contributing differently to toxicity and with different fate in

the environment. So, we can't include WET in the typical way of doing LCIA on ecotoxicity. However, there might be two ways of including WET, i.e. introducing two "new" ecotoxicity impact sub-categories:

- Acute freshwater WET
- Current exposure chronic freshwater WET

An impact category on acute ecotoxicity is typically not included in (generic) LCIA due to the in many cases small fu with related emissions (i.e. potential impacts) spread out in time and space with unknown exact location leading to the fact that only chronic ecotoxicity is relevant. In the case of NEPTUNE and LCA on WWTTs we actually have a significant point emission, i.e. the treated waste water leaving the waste water treatment plant (WWTP). So, in this case we might argue that possible acute impacts from the emitted treated waste water might be important, especially if site-specific LCIA is introduced. EDIP97 is one of the few existing LCIA methods that include acute aquatic ecotoxicity, but based on a single substance approach as described in Chapter 3 for both EDIP97 and the new developed EDIP 200X. Acute WET might be used as a substitute for the sum of the single substance acute toxicity and this type of impact category is at least in this connection independent of fate. However, even though we might have good WET data on the waste water effluent we most probably miss these data on upstream and downstream emissions (e.g. water emissions from flue gas cleaning related to electricity production), leading us to rely on single substance characterization for the two latter emissions (introducing possible bias in the comparison). Further, we might not even know the emission distribution, i.e. whether or not significant point sources are included or not in upstream and downstream processes, and therefore the relevance of including acute impacts for up- and downstream emissions. Including acute impacts might therefore be most relevant when comparing similar WWTTs mainly differing in emissions related directly to the WWTP (e.g. in case of process optimisation).

A special thing about doing LCA on municipal waste water treatment as in NEPTUNE is that the object of investigation, i.e. the treatment technology/plant in function and full scale, typically emits treated waste water continuously. The novel impact sub-category "current exposure chronic freshwater WET" might therefore be introduced. As for the acute impact category it is also independent of fate of the emission as we might characterise it by a continuous exposure of the recipient biota. This impact category is evidently only relevant for continuous waste water emissions (WWTP effluent and maybe waste water effluent from flue gas cleaning in connection with incineration of sludge and more) but can't substitute the traditional single substance based chronic ecotoxicity impact categories. Further, besides the bias problem with introducing single substance data we are here facing the same problems with unequal data availability and restrictions on usability as for the "acute freshwater WET" impact category.

Of the WET tests done within the NEPTUNE test program (Lachmund et al. 2007) tests results on mutagenicity and cytotoxicity are on/off tests and therefore not feasible to include in the (quantitative) LCIA approach used here. Further, as positive results in these tests are severe, an actual occurrence would most possible lead to an exclusion of the actual WWTT (or treatment settings etc.) making the results non-relevant for the LCA-based sustainability assessment. No WET tests for acute toxicity are explicitly included in the NEPTUNE test program, so the benefit of the proposed "acute freshwater WET" sub-impact category will be limited. The chronic flow through tests on duckweed, worms (*Lumbriculus*), mud-snails, insects (*Chironomus*) and fish will apparently not result in ECx (e.g. EC50) and NOEC values which might be used for estimating "current exposure chronic freshwater WET" ecotoxicity characterization factors based on the principles described in Chapter 3 excluding the fate part.

So, except for the YEAST tests all other ecotoxicity WET tests included in the NEPTUNE project is (only) designed and performed to determined whether or not there is a statistically

significant difference between the response of the test organism to treated as compared to untreated waste water regarding a certain end-point. So, the results from these tests are only expressed in a statement of “yes” or “no” regarding a statistically significant difference in response between the sample and a control or between samples, i.e. the results are only expressed in nominal scale (Oehlmann et al. 2009).

However, the results of the yeast screening tests for (anti-) estrogenicity (YES), (anti-) androgenicity (YAS) are expressed in equivalents of a known relevant endocrine disruptor regarding the endpoint. For example for estrogenicity the results are expressed in 17-beta-estradiol equivalents (EEQs) making it (at least in theory) possible to estimate a characterization factor regarding “current exposure chronic freshwater WET” for this type of WET. A useable relation/correlation between the measured “endpoint” (expressed in e.g. estradiol equivalents) and a population relevant endpoint (e.g. sex-ratio) for estradiol might be anticipated. This issue as related to the PNEC based EDIP97 LCIA methodology is further investigated below.

5.1 LCIA characterization of WET regarding estrogenicity

Many substances are characterized by more than one toxic mode of action (TMoA) as besides the non-specific narcotic toxic mode of action, specific types like for example estrogenicity (or other types of endocrine disruption) or cholinesterase inhibitor (e.g. insecticides) may be involved. When estimating chronic ecotoxicity characterization factors according to the PNEC-based EDIP97 methodology (see Chapter 3) the effect part (i.e. the EEI) is equal to $1/\text{PNEC}$. But for substances with more than one TMoA also more than one “PNEC” may exist if defined according to each TMoA. However, typically the PNEC of a substance is defined by the most potent TMoA even though other mode of action may be present. This is for example reflected in the report on proposed environmental quality standards (EQS) for 52 known EDSs from the German Federal Environment Agency (Moltmann et al. 2007) where only 31 EQSs (“PNECs”) is actually based on the EDS TMoA end-point. So, by introducing WET test results on estrogenicity in the LCIA characterization of chronic ecotoxicity impact potentials (i.e. characterization factors) we should be aware that we only cover this specific TMoA of the involved substances and not other TMoA that might be more potent/severe. We can't therefore exclude all known estrogenic substances in the single substance part of the LCIA. On the other hand by introducing WET on estrogenicity we may cover all occurring estrogenic activity in the “mixture” and hereby catching/including some toxicity that isn't including if only the single substance approach is used.

Estrogenicity measured in the YES test is typically expressed in units of estradiol equivalents (EEQs). The relative estrogenic potencies (REP) of different estrogenic substances as regards the YES test and determined in different studies are shown in Table 5.1.

The highest PNEC values in Table 5.1 for E2 and EE2 and the values for E1 and E3 are estimated on basis of fish NOEC values with the end-point sex-ratio as argued for in Chapter 4.

That natural (and synthetic) steroid hormones in many cases are the overall dominating contributors to observed estrogenic activity in especially municipal waste water is documented in many studies (Aerni et al. 2004, Nelson et al. 2007). Estradiol and its two metabolites estriol and estrone is typically found in the highest concentrations but due to the much lower (YES) potency (see Table 5.1) the contribution from estriol to the estrogenic activity is minor as compared to the others. The synthetic steroid hormone EE2, which is used as contraceptive agent, is in many cases not found (i.e. below detection limit, e.g. 0.1-1 ng/L) or found in concentrations at least 10 times lower than the other steroids (Clauson-Kaas et al. 2006, Aerni et al. 2004). However, EE2 is at least ten times more toxic, as reflected by the PNEC values shown in Table 5.1. However, in mixed industrial and

municipal waste waters non-steroids like nonyl phenol (and its ethoxylates) and bisphenol A may also play an important role.

Table 5.1 Relative estrogenic potencies (REP) from YES studies, and PNECs for some known estrogenic substances

Substance	YES (REP)	PNEC (ng/L)
Estradiol (E2)	1	2.4 ^b ; 0.5 ^c
Estrone (E1)	0.38 ^a	3.6 ^d
	0.29 ^e	
	0.18 ^h	
Ethinylestradiol (EE2)	1.19 ^a	0.06 ^b ; 0.03 ^c
	0.88 ^e	
	0.7 ^f	
	0.79 ^h	
Estriol (E3)	2.4E-3 ^a	670 ^d
Nonylphenol	2.5E-5 ^a	330 ^b ; 3.3 ^c
	7.2E-7 ^f	
Bisphenol A	1.1E-4 ^a	0.8 ^c

^a Rutishauser et al. (2004) ^b Clauson-Kaas et al. (2006) ^c Environmental Quality Standard (EQS) from Moltmann et al. (2007) ^d This study: Based on NOEC values of 36 ng/L (estrone) and 6700 ng/L (estriol) regarding the end-point sex ratio and reported in DRP from OECD (2004) ^e Stuer-Lauridsen et al. 2005 ^f Folmar et al. (2002) ^g Based on *in vivo* male fish VTG production study: Folmar et al. (2002) ^h Calculated on basis of data in Schultis and Metzger (2004)

As a first preliminary proxy it may therefore be assumed that the dominating estrogenicity of municipal waste water can be characterized by the presence of E1, E2, EE2 and E3. Further, average or typical concentration of these steroids in WWTP effluents may be used for the estimation of this proxy WET_{YES} characterization factor. Recently a review paper including average WWTP effluent concentrations for a high number of WWTPs/studies was published (Miege et al. 2009). Median effluent concentrations of 10 ng/L (E1), 1.5 ng/L (E2), 0.5 ng/L (EE2) and 1.4 ng/L (E3) are stated in this review. These figures are within the ranges found in other studies not included in the review like the Danish survey of estrogenic activity including Danish WWTPs (Stuer-Lauridsen et al. 2005).

The only study referred in Table 5.1 that includes determinations of REPs for all the steroids to be included is Rutishauser et al. (2004) and these REPs are therefore used. Combining these REP figures with the PNEC values based on sex ratios in Table 5.1 and the median flow concentrations a potency and concentration weighted average “1/PNEC” for YES results may be estimated, see Table 5.2.

Table 5.2 YES test equivalents (EEQs) and “occurrence weighted 1/PNEC-values” for the anticipated average waste water effluent composition

	REP	Anticipated occurrence (ng/L)	YES (ng EEQ/L)	PNEC (ng/L)	1/PNEC (L/ng)	Weighted 1/PNEC
E1	0.38	10	3.8	3.6	0.28	2.8
E2	1	1.5	1.5	2.4	0.42	0.63
EE2	1.19	0.5	0.6	0.06	17	8.3
E3	0.0024	1.4	0.0034	670	0.0015	0.0021
Total			5.9			11.7

The total weighted 1/PNEC-value of 11.7 may be divided by the total YES response of 5.9 ng EEQ/L leading to an effect indicator value of 2.0 L/ng EEQ for the YES test. This figure equals an average weighted “PNEC” value of 0.5 ng EEQ/L. Based on these results a

“current exposure chronic freshwater WET” or a WET_{YES} characterization factor may be estimated. As both the fate factor (f) and the biodegradation factor (BIO) for currently exposure equals 1, the EDIP 97 characterization factor becomes equal to $1/PNEC$:

$$ECF (WET_{YES}) = f \cdot BIO \cdot 1/PNEC = 1/PNEC = 2.0 \text{ L/ng EEQ} = 2,000,000 \text{ m}^3/\text{g EEQ}$$

Using the alternative and lower PNEC values reported in Table 5.1 (instead of the sex ratio based) does only increase the ECF (WET_{YES}) by a factor of 1.9 (3.8E6 instead of 2.0E6). If also the REPs used are substituted with the lowest ones reported in Table 5.1 the factor is increased to 3. Even by increasing the anticipated concentration of EE2 (the most potent one) to the max. value observed in effluent from waste water treatment plants according to the review by Miege et al. (2009), i.e. 5 ng EE2/L, the ECF (WET_{YES}) becomes 7.7 E6 instead of 2.0E6, that is only a factor of below 4 in difference.

By use of coming NEPTUNE laboratory test data it will probably become possible to analyze the degree of accordance of the achieved impact potential from using this preliminary proxy ECF (WET_{YES}) characterization factor with the impact potential achieved by using the single substance approach (knowing the waste water concentrations of at least the domination estrogens and assuming additivity).

It should however be stressed that the proposal presented here on how to include WET test results on estrogenicity in LCIA is only a preliminary proxy and until it have been tested and further analyzed it is recommended to use the single substance approach instead whenever possible. If data on the estrogenic steroids is missing the proxy may be used as an alternative.

One of the main problems with using an characterization factor like the developed ECF (WET_{YES}) is that it is based on test results from *in vitro* tests and many studies have shown that prediction of *in vivo* test response (e.g. VTG production) on the basis of *in vitro* test results (e.g. YES) is extremely difficult (Aerni et al. 2004, Folmer et al. 2002). That the connection between VTG induction and population relevant end points (like sex ratio) is not clear (see Chapter 3) makes the problem even more complicated.

To further illustrate how complex the area of estrogenicity is a study on feminization of wildlife fish in 51 British rivers have recently been published (Jobling et al. 2009): Statistical analysis (PCA and more) on waste water effluent concentrations of estrogen steroids, YES, anti-YAS and nonyl phenols, and indicators of feminization (i.e. VTG levels, oo-cytes in testes and more) in downstream wild-life male fish, shows that unknown anti-androgenic substances may play an important role in the sexual disruption of male fish. Furthermore, the estrogenic activity (measured by YES) did not show any good correlation with the feminization indicators which on the contrary was the case for measured concentrations of estrogen steroids and anti-YAS.

Investigating the possibilities and consequences of including anti-YAS WET test results (units of flutamide-equiv.) in the LCIA characterization of the end-point feminization (related to population sex ratio) could be a future way of further elaborate on the issue of including WET in LCIA.

As shown above the inclusion of WET in general and especially regarding EDS in the characterization step of LCIA is certainly in need of more clarity regarding correlation between measured indicator values (like EEQ) and population relevant end points. New results within this complex area will hopefully illuminate some of the essential problems making it possible to include WET in LCIA in a lot more reliable and consistent way.

6 Pathogens

One of the focus areas of the NEPTUNE project is pathogen removal. Since LCA does not currently include pathogens neither in the inventory nor in the impact assessment (Larsen et al. 2007), there is a need to develop methods to take pathogen reduction into account when performing LCAs in order to include all relevant aspects of the WWT technologies. Below is a first simple proposal on how to include pathogens in life cycle impact assessment (LCIA). The proposal is developed within the time and resource constraints on this issue within NEPTUNE and needs for further developments/improvements are pointed out.

6.1 Pathogens in waste water

Municipal WWTPs are designed to handle waste water, in which there is a high occurrence of micro-organisms excreted from humans and animals. They contribute to a mixture of pathogenic and non-pathogenic microbes in the coastal and fresh waters. The microbes derive also from other sources such as the population using the water (particularly recreational activities), farming activities, industrial activities and wild-life in addition to indigenous micro-organisms (DEPA 2001). However, the sewage effluent contribution is important because it contains organisms that are infectious via water with a low infectious dose and which are excreted in large amounts.

The Australian guideline for water recycling (NRMMC 2006) contains a list of micro-organisms of concern in raw sewage. These can roughly be divided into bacteria (*Salmonella*, *E. coli* etc.), viruses (enterovirus, adenovirus etc.), protozoa (*Cryptosporidium*, *Giardia* etc.) and helminths (*Taenia*, *Trichuris* etc.). Most of the pathogenic organisms cause gastro-related diseases with diarrhoea and vomiting, though other types of diseases may occur (e.g. respiratory illness, skin infections etc.). The Australian guideline requires identification of the occurrence of the pathogens as a reference pathogen for each group (i.e. a bacteria, a virus, a protozoa and a helminth) because characteristics, behaviours and susceptibilities of each group of organisms varies to treatments processes, i.e. different treatment processes have different efficiencies, e.g. ozonation and chlorination works well for bacteria whereas protozoans are best treated with membrane filtration or reverse osmosis (NRMMC 2006). This guideline further specifies recommendations for specific pathogenic organisms that may serve as references. Danish studies have found that the most relevant pathogens are probably *Salmonella*, *Campylobacter*, *Cryptosporidium* and *Giardia* (DEPA 2001). Anyway, most often only bacterial (*E. coli*) indicator organisms are used.

6.2 Impacts of pathogenic organisms in waste water

The assessment of potential impacts of pathogenic organisms in waste water can be considered parallel to a normal risk assessment process, i.e. containing the steps of hazard identification, dose-response, exposure assessment and risk characterization. The hazard identification reflects the issue of what are the microbial hazards (i.e. which organisms and which diseases, severity of the diseases) and what is the variability of the hazard (e.g. fluctuations in concentrations). The previous section addresses these issues.

6.2.1 Dose-response (theoretical infectious dose)

The dose response for an exposure to pathogens depends on the type of pathogen. The doses associated with infection are typically much lower for viruses and protozoa than for bacteria. Ingestion of 1-10 pathogenic viruses or protozoa causes a high likelihood of infection whereas an average of about 100 bacteria is needed (NRMMC 2006). The Australian guideline (NRMMC 2006) presents some models for the dose response relationships for different reference organisms. However, to provide an overview and perhaps also sufficient for a simplified assessment in LCA, the theoretical infectious doses are provided in Table 5.1.

Table 5.1 *Theoretical infectious doses, copied from DEPA (2002) but taken from several references*

Organism	Infectious dose, ID ₅₀
<i>E.coli</i>	< 100
<i>Salmonella</i>	1-10¹¹ (mean 10²)
<i>Campylobacter</i>	500-800 org.
Enterovirus	1-10 particles
<i>Giardia</i>	25-100 oocysts
<i>Cryptosporidium</i>	10-100 oocysts

The counts made in the NEPTUNE project encompass coliform bacteria (including *Escherichia* (*E. coli*) but also e.g. *Klebsiella*, *Citrobacter* and *Enterobacter*), *E. coli*, enterococci and bacteriophages (Lachmund et al. 2007). No information can be found on infectious dose of coliform bacteria as such but *E. coli* is a representative for that group. *Enterococci* (formerly *streptococci*) are common bacteria in the intestinal tract and is a well known for infections acquired at hospitals (nosocomial infections). It can lead to urinary infections, infections of wounds etc. (Fraser et al., 2008). However, infections via the environment is not really mentioned which is perhaps the reason why the infectious dose is not available. It will be assumed that the infectious dose correspond to that of *E.coli*. Bacteriophages only use bacteria as hosts for replication and as such are mostly used as indicator for faecal pollution (with bacteria). There is no direct correlation between the number of phages and enteroviruses. However, since they share many properties with human viruses they serve as good models for enteroviruses regarding the effect of treatment and behaviour in the water environment (WHO, 2004).

The dose-response is a result of complex interactions between pathogens and the host (the exposed human) where several factors have a large influence on whether a disease will occur or not. These factors include but are not limited to:

- The infectious dose (or hazard)
- Resistibility of the host (immunity, age etc.)
- Infectious pathway
- Exposure – time, amount, frequency
- Production of gastric acid
-

Therefore it is very difficult to give a clear indication of the number of diseases resulting from a potential exposure to the four indicators used in NEPTUNE. However, the number used will be for the coliform bacteria and for the enterococci both with a theoretical infectious dose (ID₅₀) of 100. The indicator bacteriophages can only be taken into account as an indicator of the efficiency of the treatment to remove enterovirus and it is not directly included in the LCIA factor for pathogens.

6.2.2 Exposure

Depending on the emission/usage of the treated waste water humans may get exposed to the pathogens by different routes. Recycling of the water e.g. for irrigation or as “grey water” may give rise to direct exposure through e.g. food. Exposure may additionally occur through the work environment either for the workers at the WWTP or for workers using recycled water. However, none of these exposure routes are currently taken into account in the NEPTUNE project. Emission to a recipient will primarily give rise to exposure through

recreational use (e.g. bathing) of the recipient, but may also be caused via the ingestion of fish and shellfish living in the recipient. After emission with the treated waste water a number of factors determine the actual exposure of humans resulting from the emission:

- Survival in the environment
- Dilution (hydrology of the recipient)
- Recreational use of the recipient

The survival in aquatic environment is generally better in marine environments than in freshwater and generally it has been observed that *E. coli* has a lower survival as compared to virus and *Cryptosporidium*, indicating that *E. coli* may be unsuitable as an indicator organism (Nasser et al. 2003). On the other hand a review of 22 epidemiological studies of recreational swimming waters, concludes that there is a causal dose-related relationship between disease incidents among swimmers and the bacterial indicator counts (Prüss 1998). Table 5.2 provides an overview of the survival in laboratory of several pathogens found in sewage. However, information on enterococci has not been found except a general notion that it has better survival than *E. coli* especially in marine waters and is more resistant to drying (WHO, 2004).

Table 5.2 *Survival of pathogens in laboratory (after Stenström 1996)*

Organism	Survival (20-30°C)	Survival (4-8°C)	Survival outside the host
<i>E. Coli</i>	2 months	3 months	Yes, growth possible
<i>Salmonella typhi</i> <i>Salmonella ssp.</i>	1-2 months 2-3 months	3 months 3-4 months	No Yes, growth possible
<i>Campylobacter</i>	14 days	?	Yes, adaption possible
Enterovirus	3 months	6 months	Yes
<i>Giardia</i>	1-3 months	2-6 months	Yes
<i>Cryptosporidium</i>	?	?	Yes

The bacterial die-off, referred to as the T90 (i.e. the time to achieve 90% mortality (or loss) of the original number of bacteria) is an important factor in the modelling of sewage effluent. Irradiance is the dominant factor in the die-off of bacterial cells but other factors play a role as well (DEPA 2002). Factors that influence the behaviour of pathogenic micro-organisms after discharge to a water body include:

- light (UV),
- temperature,
- salinity,
- predation,
- nutrient deficiencies,
- oxygen and redox conditions
- toxic substances,

- settling of the organism populations after discharge,
- resuspension of particles with associated sorbed organisms and
- aftergrowth, i.e. the growth of organisms in the body of water.

Some studies shows that sediments may act as reservoirs for micro-organisms implying an increased risk of exposure because of resuspension, e.g. because of human recreational activities (Craig et al. 2003, Craig et al. 2004).

Another important factor for the exposure of humans is the hydrology at the site of discharge. Hydrological condition may transfer high concentration of the micro-organisms to areas that are not in the vicinity of the discharge. However, such conditions are very difficult to handle in a generic framework for LCIA.

Other uses of the treated waste water and sludge may give rise to other exposure scenarios the relevance of which may be considered in the further development of the framework.

A fundamental difference in the interpretation of risks from chemical exposures and microbial exposures is that although symptoms of microbial illness can be acute or chronic – in risk management terms microbial risks are considered to have arisen from acute exposures. In contrast, most chemical related risks are due to low concentration long-term exposures (WHO 2001). In addition to the normal key terms hazard and exposure especially one additional term is important considering microbial risks – this is *events*, which is an occurrence that leads to an increase in the risk of exposure. An example could be a storm that leads to discharge of faecal material into a bathing area because of overflow. However, in LCA most often only normal operation is considered – accidents and risk of accidents are only seldom considered due to the difficulties quantifying these. There may be a significant variation in the hazard concentration e.g. seasonal, location and size dependent variation.

Exposure may be handled through modelling of default scenarios e.g.:

- Discharge in vicinity of areas with recreational use of water bodies
- Discharge in non-recreational areas
- Agricultural sludge application/recycling of water

However, in the NEPTUNE project time has been rather limited in terms of the efforts to develop further the exposure scenarios. In order to provide an estimate of the potential exposure it is therefore chosen to only deal with a generic situation where the discharges occur in vicinity of areas with recreational use of water bodies. Some discharges will of course occur in water bodies not used for recreational activities but there will still be a potential for dispersion to other areas. Therefore, they are treated equally.

The reason for only considering bathing water is that most literature (except for the potential use of cleaned waste water for irrigation or even drinking water) emphasizes bathing as the most common exposure route.

Discharge in vicinity of areas with recreational use of water bodies is partly regulated by the EU bathing water directive (2006/7/EEC) which gives quite strict guideline for “good quality” bathing water namely 400 enterococci/100 ml and 1000 *E. coli*/100ml in inland waters, and 200 enterococci /100ml and 500 *E. Coli*/100ml in coastal waters, respectively. Considering that the effluent pipes will not be directly at the site of bathing some dilution of the pathogen containing waste water is to be expected as was also shown in hydrological modeling in South Wales (Harris et al, 2004) where the concentration was very high in the immediate surroundings of the spill but was less than half about 500 m away. A mixing zone can therefore be defined where bathing is not recommended and a default dilution factor can be applied to indicate the worst case exposure to bathers. Normally dilution factors of 5-20 or 10-50 for freshwater lakes and coastal water, respectively can be used (Tørsløv et al, 2002).

The default dilution factor in this project will be 15. Thus all emissions of pathogens are diluted 15 times before entering a potential recreative area. No account will be taken to consider the survival of the microorganisms.

Although some exposure and diseases may arise as a consequence of small wounds etc. on the skin, it has been chosen only to consider exposure via ingestion of water during recreational activities.

A paper by Dufour et al (2006) estimates the average intake of water during swimming in a pool, but it is assumed that these values can be extrapolated to sea and freshwater bathing as well. In their estimates an adult will ingest app. 16 ml and a child app. 37 ml during swimming for 45 min.

It will be assumed that 5000 people will bathe each day for a period of 90 days (during summer time) and that 50% are children and 50% adults. Additional recreational activities such as surfing etc. that can go on for longer periods are not considered. This is clearly a very crude assumption which could be qualified through a comprehensive overview of bathing waters in Europe, the frequency of their usage, their proximity to effluent pipes etc. However, this has not been carried out in the current context.

In summary the exposure involves the following elements:

- Dilution after discharge – 15 times
- 2500 children + 2500 adults exposed in 90 days equals 225,000 children exposed and 225,000 exposed adults
- Ingestion of 16 ml water pr. adult and 37 ml water pr. child. Since they are equal in number an average intake is 26.5 ml

6.2.3 Risk characterization

Acceptable risk from microbes has traditionally been defined at a maximum level of infection or disease, e.g. one infection per 10,000 people per year (NRMMC 2006). This however, does not account for varying severity of the diseases. Australia therefore proposes to measure risk in Disability Adjusted Life Years (DALYs) (NRMMC 2006). This measure for human health is also increasingly being used in LCIA. The DALY is one of several measures that have been used in public health to measure the impact of disease, but the concept is relatively new to the area of waterborne disease risk assessment. The DALY incorporates two aspects of disease:

- The disability weight - a measure of severity of illness assessed on a scale of 0 to 1, with 1 representing the most severe health outcome (usually death)
- The duration of the health effect in years

These two figures are multiplied to give the DALY value for an individual case of disease, and the DALY values for all cases occurring as a result of population exposure are summed together to give a measure of the burden of disease attributable to a specific pathogen or chemical exposure. The time component of the DALY may be divided into Years of Life Lost (YLL) and Years Lived with Disability (YLD) to distinguish mortality and morbidity.

To keep thing still a bit simple the only diseases taken into account in the NEPTUNE project is mild diarrhoea (lasting for 3 days) and severe diarrhoea (lasting for 7 days) which have severity ratings of 0.1 and 0.23, respectively (NRMMC, 2006). The Australian guideline (NRMMC 2006) further exemplifies by Rotavirus that it will cause mild diarrhoea in 97.5 of the cases and severe diarrhoea in 2.5% of the cases. Since we do not know the full extent of pathogens in the waste water but only the indicator values (*E. coli* and enterococci) the

example of rotavirus will be applied to be general. The DALYs per case of illness can thus be calculated (NRMCC, 2006):

$$(0.1 \times 3/365 \times 0.975) + (0.23 \times 7/365 \times 0.025) = 0.00080 + 0.00011 = 0.00091 \text{ DALY pr. case}$$

6.2.4 LCIA characterization factors

Initially it was attempted to use the ID₅₀ of 100 for both *E. coli* and enterococci, i.e. an exposure to 100 bacteria will cause disease in 50 % of the cases. Since each person ingest 26,5 ml 50% of the persons should be diseased if the count is 377 pr 100 ml. Since this is even below the rather strict water quality criteria for EU (200 and 400 for enterococci and *E.coli*, respectively) it did not seem reasonable to use the infectious dose of 100 for the bacteria.

Instead, the characterization factor is based on the assumption that the EU criteria is based on an acceptable risk of 1 infection per 10,000 people per year. Thus 200 enterococci per 100 ml and 400 *E.coli* per 100 ml will cause one infection per 10,000 people.

With a dilution factor of 15 a bacterial count of 100 per 100 ml corresponds to a concentration in the bathing waters of 6.7. Assuming that the dose-response curve for bacterial infections is linear this will cause the following number of infections per year:

- *E. coli*: $450,000 / (400 / 6.7 \times 10,000) = 0.75$ infections per year
- Enterococci: $450,000 / (200 / 6.7 \times 10,000) = 1.5$ infections per year

Taking the DALY per case calculated above (0.0009) the LCIA characterization factor for bacterial count in the effluent is:

- $0.75 \times 0.00091 = 0.00068$ DALY per 100 *E. coli* per 100 ml
- $1.5 \times 0.00091 = 0.0014$ DALY per 100 enterococci per 100 ml

As an example it may be shown that in a specific case of conventional treated waste water, based on the data from the NEPTUNE wetland campaign 2008 (to be published in deliverable D3.3), i.e. 64,500 *E. coli*/100 ml and 5,100 enterococci/100 ml, the pathogen impact potentials becomes:

E. coli: $(64,500/100) \times 0.00068 = 0.44$ DALY
 Enterococci: $(5,100/100) \times 0.0014 = 0.071$ DALY

7 Site-dependent assessment

Due to the holistic approach (i.e. integrating in time and space) in LCA the assessment is typically done in a generic way and site-specific issues are only included in special cases. However, in the case of doing LCA on WWTTs it might be relevant to include site-dependent assessments at least as related to the type of recipient receiving the waste water. Other site-dependent issues may also be included in the NEPTUNE sustainability assessment, like country dependent power-scenarios, but these issues are not included here. Here we will concentrate on the potential impacts related directly to the emission of the waste water. For emission of waste water at least two main site-dependent scenarios are relevant:

- Direct emission to freshwater
- Direct emission to marine water (coastal water)

The impact categories of special interest in this case are:

- Acute and chronic ecotoxicity
- Eutrofication/nutrification

The EDIP97 methodology (Hauschild and Wenzel 1998) including its revision in 2003, i.e. the EDIP2003 methodology (Potting and Hauschild 2005a, 2005b), already comprises a way for including spatial differentiation. For example for ecotoxicity it is described how to change redistribution factors regarding air emission (depending on proportion of land as compared to surface water in the region) leading to the introduction of site-dependent exposure factors (EEF) for the aquatic and terrestrial compartments: $f \cdot \text{BIO} \cdot (1/\text{PNEC}) \cdot \text{EEF}$. Exposure factors varying according to geographical changes in biodegradation (environmental temperature) and sedimentation (salt water or freshwater) have also been developed. These factors are defined for river/lake (freshwater), estuary (brackish/salt water) and sea (salt water). Geographically there is only a distinction between Nordic countries, Western countries, Eastern countries and Southern countries in Europe. Unfortunately, corresponding normalization references does not exist. But, as already shown in Chapter 3, a distinction between direct emission to freshwater and marine water will be included in NEPTUNE together with a special waste water related sub-impact category on freshwater ecotoxicity, i.e. the “current exposure freshwater WET” as described in Chapter 5.

As regards eutrofication/nutrification a site-dependent approach including site-dependent exposure factors for 32 European countries/regions have been developed in connection with the upgrading of certain parts of the EDIP97 method to EDIP2003. These factors are estimated by use of an integrated assessment model to analyse and evaluate strategies to reduce nutrient loading of inland waters and coastal seas in Europe. The name of the model is “Cause effect Relation Model to support Environmental Negotiations (CARMEN). This model (version 1.0) is calculating the change in nutrient load in inland waters and coastal seas on basis of emissions from e.g. agriculture and municipal waste water treatment plants (Potting and Hauschild 2005a, 2005b). These site-dependent exposure factors might be included in the LCIA of NEPTUNE when dealing with site-dependency or sensitivity analysis.

Even though inland freshwater lakes are often limited by phosphorus, as is the case for many oligotrophic lakes containing excess of nitrogen (Wetzel 1975) and if the N/P ratio is above 25 (mole/mole), nitrogen limitation also exist in some freshwater lakes. Actually, if the N/P ratio is below 10 the biomass of algae is better estimated on basis of the nitrogen amount (Sand-Jensen 2000). The limiting nutrient may also change during the year (e.g. summer as compared to winter). Further, parts of the emitted nitrogen to inland freshwater will sooner or later reach coastal areas of marine water, which is typically limited by nitrogen availability. Inclusion of site-dependency regarding nutrient limitations will therefore only be included in NEPTUNE on a case-by-case principle and/or included in sensitivity analysis.

8 Land use

In the few existing LCA cases on waste water where land use has been included it has been as square meter occupied or square meter occupied times years of occupation (Larsen et al. 2007). The method development for this impact category is going in the direction of damage modelling (biotopes, biodiversity) but it is far from matured to the same degree as the other existing impact categories included in NEPTUNE. Even though it might have some relevance for especially (constructed) wetlands it is recommended not to develop new methodology on this impact category within NEPTUNE as it will most probably take up too much time and effort as compared to its overall relevance.

Land use may be included in NEPTUNE as square meter occupied times years of occupation ($\text{m}^2 \cdot \text{year}$). However, as wetlands most probably are not going to be included in the LCA part (due to lack of relevant data) the relevance of an impact category on land use is significantly diminished.

9 Land fill

The impact assessment of emissions of toxic substances from landfills, e.g. metals from flue gas cleaning products or ashes from incineration of sewage sludge, or PCBs from old electronics, is controversial in LCA. These substances typically leach very slowly from the landfill, and often, emissions to the environment will not occur before the collection of leachate ceases in the future. The slow leaching means that leachate concentrations are low – often far below predicted thresholds of effects in the surrounding environment. On the other hand, the total amounts leaving the landfill may be considerable in the very long time perspective, and this gives problems in the life cycle impact assessment where impacts are normally aggregated over time due the focus on mass flows (total emitted quantity per functional unit). One gram of a toxic chemical emitted to water thus has the same impact score regardless whether it is emitted as a pulse (in seconds) or slowly over thousands of years. LCIA's focus on the emitted mass, not on the concentration, disregards the temporal course of the emissions (the different "dilution in time"), which introduces a strong bias between landfill processes, emitting over centuries or millennia, and all the other processes in a product life cycle, which typically emit over seconds to hours or days.

Long term emissions are only relevant for the very persistent substances in waste and residual products like sewage sludge, i.e. the metals and some highly persistent organic compounds, since all non-persistent organic substances are expected to be degraded in a landfill within the first 100 years.

The uncertainty in predicting the emissions occurring after the foreseeable future is very large. The decomposition of highly persistent substances and materials in a landfill is influenced by the physical and chemical conditions in the landfill, and these will change with time under influence of different parameters. In the very long time perspective (centuries or millennia) two parameters are decisive for the future emissions of persistent pollutants from the landfill:

- The future management of landfills by human society
- Geological processes occurring at the landfill site – processes like coastal erosion, glaciers or earth quakes

The uncertainties in these two parameters are so large in the long time perspective that it is meaningless to apply some average situation and try to model long term emissions for this since the variation in emissions from a worst to a best case will be very large. Instead, we propose to circumvent the modelling uncertainties for the long time emissions without omitting the potential impacts, they may have for the LCA, by creating a new impact category which we call "stored toxicity".

9.1 Methodology

Initially, a distinction between short term emissions (< 100 years, "foreseeable future") and long term emissions (in principle indefinite time horizon) is introduced. The emissions occurring within the foreseeable future are treated together with emissions from all the other processes of the WWTP system, e.g. transport, establishing and operation of WWTPs, electricity production and production of auxiliary chemicals.

9.2 Inventory

All residual substances predicted to be present in the landfill after 100 years (for the metals typically more than 99%), regardless their speciation, are considered potential emissions contributing to the stored toxicity categories:

- Stored ecotoxicity

- Stored human toxicity

9.3 Characterization

For these two impact categories, the characterization applies the ordinary characterization factors for ecotoxicity and human toxicity of the substances in question in the EDIP97 or EDIP200X methodology. The impact scores for the stored toxicity categories represent the impacts that may happen in the long term, if all remaining toxicity in the landfill is released. Here, a coastal landfill will probably represent a different situation from an inland landfill both in terms of the environmental compartments which become affected and the nature of the geological processes that may cause the future releases. Again, this is not something we can know much about, so, a division of the emissions between 50% going to water and 50% going to surface soil to allow the scores to reflect the toxicity potentials in both of the major environmental media is assumed.

9.4 Normalization

For the use of the new impact categories together with the existing impact categories of the EDIP97 LCIA method, there is a need for normalization references in order to allow comparison to other impacts from the product system. The inventory for a set of Danish based normalization references has been established based on mass flow analyses of substances in all major waste streams containing significant amounts of persistent hazardous substances, which were land filled in Denmark in the year 1994 (the same reference year as applied for all other impact categories in EDIP97 – see Stranddorf et al. (2005a). Wastes included were slag and ashes from waste incinerators and coal-fired power plants, impregnated wood, tar, and polluted soil among others (Hansen et al. 2004). The stored ecotoxicity of the inventoried substances was determined applying the EDIP characterization factors for chronic aquatic and terrestrial ecotoxicity as shown in Table 9.1 and for human toxicity via water and soil in Table 9.2. Finally, the normalization references were expressed as person equivalents by dividing by the number of inhabitants in Denmark in 1994 in accordance with the EDIP methodology (Wenzel et al. 1997).

9.5 Weighting and interpretation

Compared to the traditional environmental impacts characterised in LCIA, the stored toxicity impacts are considerably more uncertain. In the first place, it is unknown, how large a fraction of the stored substances will ever be released to the environment – the stored toxicity potential thus represents the worst case where everything is released. Secondly, the temporal course of the emissions still remains unknown. They may occur suddenly as consequence of some geological event, but a large fraction of the release is likely to occur through gradual leaching over thousands of years at very low concentrations, which may not be able to cause any effects in exposed individuals or ecosystems. This should be taken into account in the interpretation of the results, and the weight assigned to these new impact categories relative to the traditional impact categories should reflect this.

As a practical approach to the interpretation of the stored toxicity scores in relation to the traditional toxicity scores (i.e. impact potentials), the following guidance is given based on our experience with the use of the stored toxicity potentials using the EDIP97 methodology:

- When stored human toxicity or ecotoxicity scores are of the same order of magnitude (i.e. less than a factor 10 higher) as the corresponding traditional impact potentials (IPs) for the other emissions from the product system (i.e. IPs for chronic ecotoxicity and chronic human toxicity), they should not be given any weight in the interpretation of the results.
- When the stored toxicity scores are between one and two orders of magnitude higher than the traditional IPs on chronic ecotoxicity and chronic human toxicity, they should

be included in the interpretation with a weight similar to that assigned to the traditional IPs.

- When the stored toxicity scores are more than two orders of magnitude higher than the traditional IPs on chronic ecotoxicity and chronic human toxicity, they should be given a high weight in the interpretation, and the traditional IPs of the short term emissions may be ignored.

Table 9.1 Normalization references for stored ecotoxicity based on an inventory for Denmark 1994, applying the EDIP97 factors for aquatic and terrestrial ecotoxicity for the stored substances, expressing the impacts as compartment volumes contaminated to the predicted no effect concentration of the substance (PNEC). The normalization reference is expressed as a person equivalent (annual impact from an average person)

Substance or substance group	Source	Amount land filled ton/yr	Stored ecotoxicity score			
			water		soil	
			m ³ water	%	m ³ soil	%
Nickel	Various (MFA)	955	$3.20 \cdot 10^{11}$	0.5	$3.34 \cdot 10^8$	12.3
Mercury	Various (MFA)	0.6	$2.40 \cdot 10^9$	0.0	$3.18 \cdot 10^7$	1.2
Cadmium	Various (MFA)	19	$1.11 \cdot 10^{12}$	1.9	$2.04 \cdot 10^8$	7.5
Lead	Various (MFA)	1550	$1.55 \cdot 10^{12}$	2.6	$7.75 \cdot 10^7$	2.9
Arsenic	Various (MFA)	64	$6.03 \cdot 10^{10}$	0.1	$1.05 \cdot 10^8$	4.0
Arsenic	Wood preservation	16	$1.52 \cdot 10^{10}$	0.0	$2.64 \cdot 10^7$	1.0
Copper	Various (MFA)	5600	$3.50 \cdot 10^{13}$	59.1	$5.60 \cdot 10^8$	20.6
Chromium	Various (MFA)	3250	$1.09 \cdot 10^{12}$	1.8	$1.63 \cdot 10^8$	6.0
Chromium	Wood preservation	20	$6.70 \cdot 10^9$	0.0	$1.00 \cdot 10^6$	0.0
PAH (benz(a)pyrene-TEQ)	Contaminated soil	0.14	$8.19 \cdot 10^{10}$	0.1	$4.55 \cdot 10^6$	0.2
PAH (benz(a)pyrene-TEQ)	Car tires	0.03	$1.56 \cdot 10^{10}$	0.0	$8.66 \cdot 10^5$	0.0
PAH (benz(a)pyrene-TEQ)	Bio ashes	0.001	$4.30 \cdot 10^8$	0.0	$2.39 \cdot 10^4$	0.0
PAH (benz(a)pyrene-TEQ)	Creosote in wood	32.5	$1.95 \cdot 10^{13}$	33.0	$1.08 \cdot 10^9$	39.9
PAH (benz(a)pyrene-TEQ)	Asphalt	0.46	$2.76 \cdot 10^{11}$	0.5	$1.53 \cdot 10^7$	0.6
Dioxin (I-TEQ)	Slag/ashes	0.00007	$9.17 \cdot 10^{10}$	0.2	$4.91 \cdot 10^6$	0.2
Total			$5.91 \cdot 10^{13}$	100	$2.61 \cdot 10^9$	100
Inhabitants DK, 1994	$5.166 \cdot 10^6$					
Normalization reference (Person equivalent, m³/pers/yr)			$1.14 \cdot 10^7$		506	

Table 9.2 Normalization references for stored human toxicity based on an inventory for Denmark 1994, applying the EDIP97 factors for human toxicity via water and soil for the stored substances. The normalization reference is expressed as a person equivalent (annual impact from an average person)

Substance or substance group	Source	Amount land filled ton/yr	Stored human toxicity score			
			Via water		Via soil	
			m ³ water	%	m ³ soil	%
Nickel	Various (MFA)	955	$9.07 \cdot 10^6$	0.00	$7.16 \cdot 10^7$	0.9
Mercury	Various (MFA)	0.6	$6.60 \cdot 10^{10}$	16	$4.86 \cdot 10^7$	0.6
Cadmium	Various (MFA)	18.5	$2.59 \cdot 10^{10}$	6	$5.18 \cdot 10^7$	0.7
Lead	Various (MFA)	1550	$2.02 \cdot 10^{11}$	49	$7.75 \cdot 10^7$	1
Arsenic	Various (MFA)	64	$1.17 \cdot 10^9$	0.3	$4.13 \cdot 10^9$	54
Arsenic	Wood preservation	16	$2.96 \cdot 10^8$	0.07	$1.04 \cdot 10^9$	13
Copper	Various (MFA)	5600	$4.76 \cdot 10^{10}$	12	$1.40 \cdot 10^7$	0.2
Chromium	Various (MFA)	3250	$2.93 \cdot 10^{10}$	7	$2.28 \cdot 10^9$	29
Chromium	Wood preservation	20	$1.80 \cdot 10^8$	0.04	$1.40 \cdot 10^7$	0.2
PAH (benz(a)pyrene-TEQ)	Contaminated soil	0.14	$2.18 \cdot 10^7$	0.01	123	0.00
PAH (benz(a)pyrene-TEQ)	Car tires	0.026	$4.16 \cdot 10^6$	0.00	23.4	0.00
PAH (benz(a)pyrene-TEQ)	Bio ashes	0.0007	$1.15 \cdot 10^5$	0.00	0.65	0.00
PAH (benz(a)pyrene-TEQ)	Creosote in wood	32.5	$5.20 \cdot 10^9$	1.3	$2.93 \cdot 10^4$	0.00
PAH (benz(a)pyrene-TEQ)	Asphalt	0.46	$7.35 \cdot 10^7$	0.02	414	0.00
Dioxin (I-TEQ)	Slag/ashes	0.00007	$3.60 \cdot 10^{10}$	9	$5.90 \cdot 10^5$	0.01
Total			$4.13 \cdot 10^{11}$	100	$7.72 \cdot 10^9$	100
Inhabitants DK, 1994	$5.166 \cdot 10^6$					
Normalization reference (Person equivalent, m³/pers/yr)			$8.00 \cdot 10^4$		$1.49 \cdot 10^3$	

9.6 Discussion

The distinction between short and long term emissions in LCA is necessary for scientific reasons, i.e. the higher uncertainties related to actual impacts of long term emissions compared to short term emissions. Furthermore, specifically for landfills there is much evidence that more than 99% of the hazardous substances still remain in the landfill after 100 years. The proposed framework/methodology introduces a simple way of handling impacts from long term emissions of metals and persistent organic compounds from landfills. Acknowledging the high uncertainties related to modelling of release from landfills the entire amounts of persistent toxicants remaining in the landfill after the foreseeable time horizon of 100 years are included and a default partitioning representing an equal split between water and soil is assumed. This represents a crude estimate of the potential impacts, but it also

ensures that they are taken into account, and the treatment in a separate impact category allows the proper weight to be given to them in the weighting and interpretation of the LCA. The alternative today is either to include them in the other emission-related impact categories (leading to a too strong focus on them), or to leave them out of the assessment by disregarding emissions occurring after 100 years. Landfills and the potential impact of these is an issue of high concern for both public and politicians, and the stored toxicity approach is at least an interim solution which may convert the problem into a weighting and interpretation problem until a satisfactory solution may be developed for the modelling problems in the inventory and characterization of these impacts.

10 Normalization and weighting

Half of the 22 existing LCA studies on WWTTs reviewed in Larsen et al. (2007) include normalization. Normalization references are typically estimated on basis of the total societal (land, region or global) potential impact (within each impact category) per citizen within a reference year. By dividing the estimated impact potentials in a case study by the corresponding normalization reference it becomes possible to express the results in person equivalents (PE) or in percentage of the total societal impact in each impact category. In this way it is possible to get an impression of the relative magnitude of the impacts. It is therefore recommended to include normalization in NEPTUNE as part of the presentation and interpretation of the sustainability studies.

Only five of the 22 reviewed existing LCA studies on WWTTs (Larsen et al. 2007) do weighting. Weighting factors are typically estimated by introducing value-choices and factors are estimated on that basis for each impact category, or factors are anticipated as part of a sensitivity analysis. By multiplying the normalised impact potential by the corresponding weighting factor a weighted impact potential result appear.

Methods for weighting can be divided into panel methods, monetisation methods and distance-to-target methods (Finnveden et al. 2006). Panel methods are typically done by asking a panel of participants (e.g. representatives of society or stakeholders) to rank and/or assign weights to different impact categories (or safeguard objectives) as done in the Eco-Indicator 99 method (Goedkoop and Spriensma 2001). The monetisation methods can be based on different principles like willingness-to-pay or taxes and fees on emissions and resource consumption as in the Eco-tax method by Finnveden et al. (2006). The distance-to-target method used as distance to political reduction targets are used in the EDIP97 method (Wenzel et al. 1997).

In the comments from the NEPTUNE advisory board after the Zürich half-year meeting (Minutes Zurich 2008) it is recommended to distinguish between weighting based on distance to political reduction targets, designated “target modification” (may be interpreted as a normalization based on a future proxy scenario) and the internal weighting based on the “importance” of the different impact categories, designated “weighting of impacts”. Even though “target modification” actually also is a “weighting of impacts” based on a kind of “importance” (as seen by the political institutions) the inclusion of other weighting principle, as mentioned above, is highly relevant. Further, the already presented idea of back calculating how much higher a weighting factor has to be in order to make weighted impacts from two different scenarios equal (e.g. ecotoxicity as compared to global warming potential) will be further included in the NEPTUNE LCIA interpretations.

The strength of using normalization and weighting is that it creates the opportunity to aggregate all the impact potentials into one common impact score and hence makes comparison between different WWTT alternatives a lot simpler. On the other hand the weakness is that weighting is based on value choices and not natural science and therefore debatable. Using different weighting principles is therefore recommended when trying to test the solidity of a result.

10.1 Coverage of the normalization reference

In the NEPTUNE project we are comparing induced impacts (typically related to building of infrastructure and operation) with avoided impacts (typically related to the removal of pollutants) of a given waste water treatment technology. The normalization references used should therefore be relevant for both types of impacts. A normalization reference on ecotoxicity only covering municipal waste water emission is therefore not sufficient as potential ecotoxic effects from other water and air emissions, due to e.g. electricity production, is not covered. The recommended normalization references to be used within

NEPTUNE are therefore the general ones aiming at covering all relevant emissions and typically used within LCA studies. For the new EDIP200X methodology on ecotoxicity these normalization references are described in Chapter 3 and for the EDIP97 methodology defined in Wenzel et al. (1997) and Stranddorf et al. (2005a).

Normalization is one of the steps that can be included in a life cycle impact assessment (LCIA), i.e. classification and characterization, which are mandatory according to ISO 14044 (ISO 2006), and normalization and valuation (weighting) which are optional steps. Weighting, which is the last step and preceded by normalization, is treated above. In order to explain normalization in a proper way all the other three steps are shortly described below.

The process of LCIA starts with *classification*: The emissions mapped in the inventory are assigned to the relevant impact categories, e.g. carbon dioxide (CO₂) and methane (CH₄) emissions are assigned to global warming potential (gwp), and micropollutants emitted via waste water are assigned to the impact category on chronic aquatic ecotoxicity (ETWC).

Then during *characterization* an impact potential (IP) is calculated for each impact category, by summing up the results of each assigned emission quantity (Q) multiplied by its corresponding characterization factor (CF) within that impact category:

$$IP_{\text{impact category A}} = Q_1 * CF_{1A} + Q_2 * CF_{2A} + \dots$$

For example for global warming:

$$IP_{\text{gwp}} = Q_{\text{CO}_2} * 1 + Q_{\text{CH}_4} * 25 + \dots$$

In this example CF_{CO₂} has the value 1 gram CO₂ per gram CO₂ emitted and CF_{CH₄} the value 25 gram CO₂ per gram CH₄ emitted, so the resulting IP_{gwp} is given in the unit gram of CO₂-equivalents. As is indicated by this example, all the characterization factors for the emitted substances contributing to global warming are expressed in units of CO₂ equivalents. In a similar way the impact potential for chronic aquatic ecotoxicity is estimated on basis of the quantity emitted of each substance (e.g. micropollutant) multiplied by the corresponding characterization factor and the result expressed in cubic meter of water, i.e. a dilution volume as explained in Chapter 3.

For each waste water treatment technology included, both the “induced impact part” and the “avoided impact part” will be represented by a collection of impact potentials (i.e. an impact profile). The “induced impact part” is typically dominated by energy-related impacts (i.e. global warming) whereas the “avoided impact part” is dominated by the reduced emission of micropollutants, i.e. reduction in chronic aquatic ecotoxicity. In order to be able to compare these two and hereby assess the sustainability of the process (i.e. do we avoid more impact than we induce?) the impact potentials may be further elaborated by use of normalization followed by weighting to assist comparisons across impact categories.

During *normalization* the impact potentials are related to reference information. In the method used in NEPTUNE this reference information is represented by the total impact potential in the reference region divided by the number of persons in the region. For example for global warming potential (gwp) the reference information, i.e. the normalization reference (NR_{gwp W1994}), is 8,700 kg CO₂-equivalents/person/year, meaning that in 1994, greenhouse gases equivalent to 8,700 kg CO₂ was emitted to air on average for each person worldwide. For chronic aquatic ecotoxicity (ETWC) the normalization reference (NR_{etwc EU1994}) in the EDIP97 method is regional (EU-15) and amounts to 7.92 * 10⁵ m³/person/year, meaning that in 1994, an amount of micropollutants representing a need of about 800,000 m³ water (roughly to reach a concentration below PNEC, but see Chapter 3 for details) was emitted to water on average for each EU-15 citizen. The normalised impact potential (NIP) is then calculated by

taking the impact potential of a given impact category (e.g. ETWC) and dividing it by the corresponding normalization reference:

$$NIP_{\text{impact category A}} = IP_{\text{impact category A}} / NR_{\text{impact category A}}$$

In this way all impact potentials may be expressed in person-equivalents (PE) or person-equivalents times year (PE*year).

For the impact category on global warming (and other non-toxic-related impact categories) the normalization reference is pretty solid and not that uncertain as compared to the impact categories on ecotoxicity (and human toxicity). As the impact categories on ecotoxicity (especially chronic aquatic ecotoxicity) is very important in the NEPTUNE project dealing with emissions of micropollutants this issue is further dealt with below.

One of the main problems regarding the normalization references for ecotoxicity is that we can only include a fraction of the total number of chemicals (i.e. micropollutants) emitted each year as not only is our knowledge of the amounts very limited but the ecotoxicity data needed for estimating the characterization factors does not exist for the major part (Larsen 2004).

It therefore becomes very important to get an indication of whether or not we have included the most important (i.e. contributing) chemical emissions and whether or not including new chemicals will have a significant impact on the size of the normalization reference.

If the normalization reference is too low (as compared to the “true” value) the impact category on ecotoxicity will due to normalization get a too high value (number of PE) as compared to the other impact categories and a bias in favour of typically the avoided impact will be introduced in our sustainability assessment of the included waste water treatment technologies. On the other hand if the normalization reference is too high the assessment will typically be biased in favour of the induced impacts.

In NEPTUNE we are focusing on “emerging” micropollutants for which no characterization factors exist and they are therefore not included in the existing normalization references in the literature. As part of the project we estimate characterization factors for these substances and they become the most important contributor to the avoided impact in many cases, e.g. ozonation and activated carbon treatment.

In order to see whether or not the inclusion of these new substances can have a significant impact on the ecotoxicity-related normalization references the potential contribution from pharmaceuticals is investigated below.

10.2 The impact on normalization by including pharmaceuticals

The aim of the study is to assess the potential influence of pharmaceuticals on the normalization references used in the EDIP97-methodology.

Both national and regional scales are assessed, namely referring to Denmark and EU-15 (based on extrapolations).

10.2.1 Methodology

The work was performed to enable the comparisons between existing impact potentials of ecotoxicity impact categories, as reported in Stranddorf et al. (2005b) (who updated normalization references for EDIP97, considering the emission year 1994), and impact potentials obtained by including “new” substances, i.e. the pharmaceuticals for which

characterization factors (CFs) have been estimated until now within the NEPTUNE project (see Table 10.1, *column 9, 10 and 11*).

Reported inventory data for pharmaceuticals consist of sales for the considered countries (*column 3* in Table 10.1). These data are based on data from three books on pharmaceuticals, i.e. “Pharmaceuticals in the environment. Sources, fate, effects and risks” (Kümmerer 2008), “Human Pharmaceuticals, Hormones and Fragrances. The challenge of micropollutants in urban water management” (Ternes and Joss 2006) and “Human Pharmaceuticals: Assessing the impacts on aquatic ecosystems” (Williams 2003).

As the aim here only is to assess whether or not the inclusion of pharmaceuticals can have a significant impact on the normalization references, a simplified conservative approach is used. It is therefore assumed that 100% of the chemicals end up in the sewer (*column 6* in Table 10.1) and that no removal at the waste water treatment plant occur (*column 7*, in Table 10.1). In short, sales are made coincide with emissions since 100% of the sold compounds are assumed to reach the environment (*column 8*, in Table 10.1). This very conservative assumption is also used for the included impact category on chronic ecotoxicity in soil ((ETSC)s), i.e. the total consumption of pharmaceuticals is emitted to soil. Even though not realistic due to its large overestimation, this approach has the advantage of illustrating the worst-case scenario when assessing the potential influence of the pharmaceuticals on the normalization references.

However, two main sources of uncertainties related to the inventory data are identified:

- Sales are not reported for all EU-15 countries. The number of reporting countries differs from chemical to chemical (*column 4* in Table 10.1) and no real comprehensiveness can therefore be achieved.
- For each compound, the reported reference years differ from one country to another (*column 5* in Table 10.1).

The sales of each compound for the reporting countries were extrapolated to obtain the ones for EU-15 (and Denmark) and the Gross Domestic Products (GDP) for EU-15 countries in 2004 (UN 2009) were used to perform this extrapolation (direct proportionality assumed). The correlation between GDP and consumptions has not been checked, but is probably fairly good in this context.

Differences related to reporting years were not corrected. The situation in 1994 is then assumed to be similar to the ones described by the defined literature sources. Though uncertainties may arise from this consideration, it is likely that the order of magnitude of the sales remained stable during the whole range of years.

Thus, following this procedure, an estimated total consumption of 3 800 tons of pharmaceuticals for EU-15 is achieved, see Table 10.1.

Table 10.1 Raw data, assumptions (conservative approach) and characterization factors (CFs) for the considered pharmaceuticals

Compound	CAS-number	Emission						CF (m ³ /g) ¹		
		Sales (kg)	Countries	Years	Input to sewer (%)	Input to water environment (%)	Input to water environment (kg)	(ETWA) _w ²	(ETWC) _w ²	(ETSC) _s ²
17 α -ethynyl estradiol (EE2)	57-63-6	8.65E+01	FI, DE, ES, SE, UK	99, 2001, 2003, 2002, 2001	100%	100%	8.65E+01	9.09E+00	1.67E+07	1.17E+04
17 β -estradiol (E2)	50-28-2	1.53E+02	SE	2002	100%	100%	1.53E+02	1.96E+00	2.08E+05	4.32E+02
Atenolol	29122-68-7	1.28E+04	SE, DE	2002, 2005	100%	100%	1.28E+04	2.99E-01	2.99E+00	6.20E-01
Bezafibrate	41859-67-0	6.61E+04	AT, FR, FI, DE, SE	97, 98, 99, 2001, 2005	100%	100%	6.61E+04	3.30E-01	4.35E+02	1.04E+03
Carbamazepin	298-46-4	1.52E+05	AT, FR, FI, DE, ES, SE	97, 98, 99, 2001, 2003, 2005	100%	100%	1.52E+05	3.16E-01	4.00E+02	6.84E+00
Clarithromycin	81103-11-9	7.16E+03	DE	2001	100%	100%	7.16E+03	2.13E+03	3.23E+03	4.63E+03
Clindamycin	18323-44-9	1.61E+04	DE	2001	100%	100%	1.61E+04	1.17E+01	1.17E+02	6.51E+01
Clofibric acid	882-09-7	1.60E+04	DE, FR	1995, 1999	100%	100%	1.60E+04	2.49E-01	4.07E+01	1.01E+02
Diatrizoate	117-96-4							9.09E-03	9.09E-02	8.55E-02
Diclofenac	15307-86-5	1.07E+05	AT, FR, FI, DE, ES, SE	97, 98, 99, 2001, 2003, 2005	100%	100%	1.07E+05	6.90E-01	1.00E+01	2.29E+01
Erythromycin	114-07-8	1.92E+04	DE	2001	100%	100%	1.92E+04	5.00E+02	5.00E+03	7.18E+03
Ibuprofen	15687-27-1	7.08E+05	AT, FR, FI, DE, ES, SE	97, 98, 99, 2001, 2003, 2005	100%	100%	7.08E+05	1.04E+00	5.21E+00	1.05E+01
Iohexol	66108-95-0							1.36E-05	1.36E-04	7.40E-05
Iopamidol	60166-93-0	4.30E+04	DE	2001	100%	100%	4.30E+04	2.65E-04	2.65E-03	3.50E-03
Iopromid	73334-07-3	2.10E+05	AT, FR, DE	97, 98, 2001	100%	100%	2.10E+05	1.00E-03	1.00E-02	1.43E-02
Metoprolol	51384-51-1	1.13E+04	DE	2005	100%	100%	1.13E+04	1.32E+00	1.32E+01	5.83E+00
Naproxen	22204-53-1	1.37E+04	SE	2002	100%	100%	1.37E+04	5.18E-01	5.18E+00	1.25E+01
Primidone	125-33-7							6.94E-02	6.94E-01	3.18E-02
Propanolol	525-66-6	3.96E+04	DE, FR	1995, 1999	100%	100%	3.96E+04	4.10E+01	2.00E+04	5.43E+02
Roxithromycin	80214-83-1	1.66E+04	AT, FR, FI, DE, ES, SE	97, 98, 99, 2001, 2003, 2005	100%	100%	1.66E+04	2.43E+01	3.56E+02	3.13E+02
Sotalol	3930-20-9	1.19E+04	DE	2005	100%	100%	1.19E+04	3.33E-01	3.33E+00	2.16E+00
Sulfamethoxazole	723-46-6	8.44E+04	AT, FR, DE, ES, SE	97, 98, 2001, 2003, 2005	100%	100%	8.44E+04	3.73E+02	1.69E+03	6.54E+02
Trimethoprim	738-70-5							1.25E-01	1.25E+00	7.86E-02

¹ The CFs presented at the NEPTUNE Varna, Bulgaria meeting, 22 October, 2008: "WP4 Status of inventories. Prioritized processes and estimation of characterization factors". HF Larsen, DTU (www.eu-neptune.org)

² Ecotoxicity water, acute, for emissions to water (ETWA)_w; Ecotoxicity water, chronic, for emissions to water (ETWC)_w; Ecotoxicity soil, chronic, for emissions to soil (ETSC)_s

10.2.2

Results and discussions

General interpretation

Pharmaceutical sales (here identical to releases) extrapolated for Denmark and EU-15 as well as corresponding impact potentials (IPs) for all three ecotoxicity-related impact categories are reported in Table 10.2.

Impact potentials for all categories usually assessed to set the normalization references of those impacts are presented in Table 10.3 to Table 10.5.

The normalization references' settings are those based on the emission year 1994. Comparisons with those relying on the year 2004 were also performed (not shown). Overall, the same conclusions apply in both cases and only the 1994 case is considered further in this discussion.

According to Table 10.3, Table 10.4 and Table 10.5 the overall result is that for all three ecotoxicity-related impact categories, the pharmaceutical substance-category is characterized by impact potentials that are a factor 10^4 to 10^5 lower than the highest substance-category impact potentials for both Denmark and EU-15 (i.e. TBT for ecotoxicity in aquatic environment and pesticides for ecotoxicity in terrestrial environment).

Thus, based on this analysis, it seems reasonable to conclude that the inclusion of pharmaceuticals has a negligible impact on the normalization references.

Table 10.2 Sales, and impact potentials (IPs) for ecotoxicity-related impacts, regarding Denmark and EU-15

Compound	CAS-number	Sales (kg) (= input to water environment)		IP (m ³ /yr) ----- DK				IP (m ³ /yr) ----- EU-15			
		DK	EU-15	(ETWA) _w ¹	(ETWC) _w ¹	%(etwc) ¹	(ETSC) _s ¹	(ETWA) _w ¹	(ETWC) _w ¹	%(etwc) ¹	(ETSC) _s ¹
17 α -ethynyl estradiol (EE2)	57-63-6	3.28E+00	1.65E+02	2.98E+01	5.48E+07	39.8%	3.84E+04	1.50E+03	2.76E+09	39.8%	1.94E+06
17 β -estradiol (E2)	50-28-2	1.07E+02	5.40E+03	2.10E+02	2.23E+07	16.2%	4.62E+04	1.06E+04	1.12E+09	16.2%	2.33E+06
Atenolol	29122-68-7	1.01E+03	5.10E+04	3.02E+02	3.02E+03	0.0%	6.27E+02	1.52E+04	1.52E+05	0.0%	3.16E+04
Bezafibrate	41859-67-0	2.87E+03	1.45E+05	9.47E+02	1.25E+06	0.9%	2.98E+06	4.78E+04	6.30E+07	0.9%	1.51E+08
Carbamazepin	298-46-4	5.58E+03	2.82E+05	1.76E+03	2.23E+06	1.6%	3.82E+04	8.90E+04	1.13E+08	1.6%	1.93E+06
Clarithromycin	81103-11-9	6.37E+02	3.21E+04	1.36E+06	2.06E+06	1.5%	2.95E+06	6.85E+07	1.04E+08	1.5%	1.49E+08
Clindamycin	18323-44-9	1.43E+03	7.22E+04	1.68E+04	1.68E+05	0.1%	9.32E+04	8.45E+05	8.45E+06	0.1%	4.70E+06
Clofibric acid	882-09-7	8.15E+02	4.11E+04	2.03E+02	3.32E+04	0.0%	8.23E+04	1.02E+04	1.67E+06	0.0%	4.15E+06
Diatrizoate	117-96-4										
Diclofenac	15307-86-5	3.92E+03	1.98E+05	2.71E+03	3.92E+04	0.0%	8.99E+04	1.37E+05	1.98E+06	0.0%	4.53E+06
Erythromycin	114-07-8	1.71E+03	8.62E+04	8.55E+05	8.55E+06	6.2%	1.23E+07	4.31E+07	4.31E+08	6.2%	6.19E+08
Ibuprofen	15687-27-1	2.60E+04	1.31E+06	2.70E+04	1.35E+05	0.1%	2.73E+05	1.36E+06	6.82E+06	0.1%	1.37E+07
Iohexol	66108-95-0										
Iopamidol	60166-93-0	3.83E+03	1.93E+05	1.01E+00	1.01E+01	0.0%	1.34E+01	5.12E+01	5.12E+02	0.0%	6.76E+02
Iopromid	73334-07-3	1.01E+04	5.07E+05	1.01E+01	1.01E+02	0.0%	1.44E+02	5.07E+02	5.07E+03	0.0%	7.26E+03
Metoprolol	51384-51-1	1.01E+03	5.07E+04	1.33E+03	1.33E+04	0.0%	5.87E+03	6.70E+04	6.70E+05	0.0%	2.96E+05
Naproxen	22204-53-1	9.58E+03	4.83E+05	4.96E+03	4.96E+04	0.0%	1.20E+05	2.50E+05	2.50E+06	0.0%	6.04E+06
Primidone	125-33-7										
Propanolol	525-66-6	2.02E+03	1.02E+05	8.26E+04	4.03E+07	29.3%	1.09E+06	4.17E+06	2.03E+09	29.3%	5.52E+07
Roxithromycin	80214-83-1	6.08E+02	3.07E+04	1.48E+04	2.17E+05	0.2%	1.90E+05	7.45E+05	1.09E+07	0.2%	9.60E+06
Sotalol	3930-20-9	1.06E+03	5.34E+04	3.53E+02	3.53E+03	0.0%	2.29E+03	1.78E+04	1.78E+05	0.0%	1.15E+05
Sulfamethoxazole	723-46-6	3.18E+03	1.60E+05	1.19E+06	5.38E+06	3.9%	2.08E+06	5.99E+07	2.71E+08	3.9%	1.05E+08
Trimethoprim	738-70-5										
Total		7.54E+04	3.80E+06	3.55E+06	1.37E+08	100.0%	2.24E+07	1.79E+08	6.93E+09	100.0%	1.13E+09

¹ Ecotoxicity water, acute, for emissions to water (ETWA)_w; Ecotoxicity water, chronic, for emissions to water (ETWC)_w; Ecotoxicity soil, chronic, for emissions to soil (ETSC)_s

Table 10.3 Impact potentials (IP) by substance-category and normalization references for the impact category on chronic aquatic ecotoxicity (ETWC) for Denmark and EU-15, year 1994 ¹

ETWC	Denmark		EU-15	
	IP _{etwc} (m ³ /yr)	% _{etwc}	IP _{etwc} (m ³ /yr)	% _{etwc}
Heavy metals ⁴	7.77E+11	19%	4.16E+13	32%
Organic compounds ⁴	3.75E+11	9%	1.89E+13	15%
Oil	Not included	-	3.63E+12	3%
TBT	2.83E+12	69%	5.38E+13	41%
Atmospheric depositions ²	1.37E+11	3%	1.24E+13	10%
Pharmaceuticals	1.37E+08	0.0033%	6.93E+09	0.0053%
TOTAL	4.12E+12	100.0%	1.30E+14	100.0%
Population 1994 ³	5.20E+06		3.70E+08	
Normalization references	7.92E+05	m³/year/capita	3.52E+05	m³/year/capita

¹ All impact potentials, but the one on pharmaceuticals, are extracted from Stranddorf et al. (2005b)

² The category “*Atmospheric depositions*” refers to airborne emissions of heavy metals, which deposit on aquatic ecosystems.

³ UN (2009) ⁴ Via waste water

Table 10.4 Impact potentials (IP) by substance-category and normalization references for the impact category on acute aquatic ecotoxicity (ETWA) for Denmark and EU-15, year 1994 ¹

ETWA	Denmark		EU-15	
	IP _{etwa} (m ³ /yr)	% _{etwa}	IP _{etwa} (m ³ /yr)	% _{etwa}
Heavy metals ³	7.88E+10	20%	4.19E+12	39%
Organic compounds ³	2.30E+10	6%	1.16E+12	11%
Oil	Not included	-	6.06E+10	1%
TBT	2.83E+11	74%	5.38E+12	50%
Pharmaceuticals	3.55E+06	0.0009%	1.79E+08	0.0017%
TOTAL	3.85E+11	100.0%	1.08E+13	100.0%
Population 1994 ²	5.20E+06		3.70E+08	
Normalization references	7.40E+04	m³/year/capita	2.92E+04	m³/year/capita

¹ All impact potentials, but the one on pharmaceuticals, are extracted from Stranddorf et al. (2005b)

² UN (2009) ³ Via waste water

Table 10.5 Impact potentials (IP) by substance-category and normalization references for the impact category on chronic terrestrial ecotoxicity (ETSC) for Denmark and EU-15, year 1994¹

ETSC	Denmark		EU-15	
	IP _{etsc} (m ³ /yr)	% _{etsc}	IP _{etsc} (m ³ /yr)	% _{etsc}
<i>Pesticides (total)</i>	3.42E+12		3.57E+14	
Fungicides	3.50E+11	10.2%	7.83E+13	21.9%
Herbicides	2.85E+12	83.5%	1.27E+14	35.5%
Insecticides	2.15E+11	6.3%	1.52E+14	42.5%
Sewage sludge for agriculture ²	1.89E+07	0.0006%	5.38E+08	0.0002%
Atmospheric deposition ³	5.90E+07	0.0017%	3.51E+10	0.0098%
Pharmaceuticals	2.24E+07	0.0007%	1.13E+09	0.0003%
TOTAL	3.42E+12	100.0%	3.57E+14	100.0%
Population 1994 ⁴	5.20E+06		3.70E+08	
Normalization references	6.57E+05 m³/year/capita		9.66E+05 m³/year/capita	

¹ All impact potentials, but the one on pharmaceuticals, are extracted from Stranddorf et al. (2005b)

² The category “Sewage sludge for agriculture” refers to emissions of metals and organics, appearing in the fraction of sewage sludge used for agriculture purposes.

³ The category “Atmospheric depositions” refers to airborne emissions of heavy metals, which deposit on terrestrial ecosystems.

⁴ UN (2009)

Influence of uncertainties due to emission data

Regarding pharmaceuticals

Besides a potential counterbalance from assuming sales identical to emissions, uncertainties are expected through the extrapolation process. However, though no quantified assessment was made, and only a fraction of the pharmaceuticals used is included, it seems very unlikely to obtain a deviation factor of 10⁴ - 10⁵ if a comparison between the extrapolated data used in this study and actual releases was possible.

To substantiate this statement, it may be pointed out that Ternes and Joss (2006) quote statistics regarding the US and Sweden (Sedlak et al. 2005, Stockholm County Council 2005), which state that, “in industrialized countries, a consumption of active pharmaceutical ingredients (a.i.) of between 50 and 150 g per capita (person) and per year are to be expected”. This leads to a maximal release of pharmaceuticals in EU-15 of 5.55 10⁷ kg/yr, that is to say 15 times higher than the amount considered in the main assessment of this study, see Table 10.2.

Table 10.6 illustrates the influence of considering this particular consumption figure for EU-15, assuming the same distribution of the pharmaceuticals as in the main assessment. Only the case of chronic ecotoxicity in aquatic ecosystems is depicted as it is the most sensitive one (comparisons of the %IP for all three ecotoxicity-related impacts; Table 10.3 to Table 10.5).

By comparing Table 10.6 with Table 10.3, it becomes evident that the “importance” of pharmaceuticals is only increased from 0.0053% to 0.0776%: therefore, this only reduces the deviation factors by one order of magnitude (logically the factor 15). Therefore, pharmaceuticals are still negligible as their contribution to the normalization references is still below 1 per thousand.

The fact, that due to metabolism in the human body, biodegradation in the waste water treatment plant and more, only a fraction of the consumed pharmaceuticals will actually reach the aquatic environment (Ternes and Joss 2006) further strengthens the conclusion that the contribution from pharmaceuticals is insignificant.

Table 10.6 Impact potentials by substance-category and normalization reference (year 1994) for the impact category on chronic aquatic ecotoxicity (ETWC) for EU-15, resulting from using the highest estimates of pharmaceuticals' consumptions, i.e. 150 g a.i./capita/year according to Ternes and Joss (2006) ¹

ETWC	EU-15	
	IP _{etwc} (m ³ /yr)	% _{etwc}
Heavy metals ⁴	4.16E+13	32%
Organic compounds ⁴	1.89E+13	14%
Oil	3.63E+12	3%
TBT	5.38E+13	41%
Atmospheric depositions ²	1.24E+13	10%
Pharmaceuticals	1.01E+11	0.0776%
TOTAL	1.30E+14	100.0%
Population 1994 ³	3.70E+08	
Normalization reference	3.53E+05	m³/year/capita

¹ All impact potentials, but the one on pharmaceuticals, are extracted from Stranddorf et al. (2005b)

² The category “Atmospheric depositions” refers to airborne emissions of heavy metals, which deposit on aquatic ecosystems.

³ UN (2009) ⁴ Via waste water

Regarding categories reported by Stranddorf et al. (2005b)

As clearly stated in Stranddorf et al. (2005b), emission data used to assess the different categories are characterized by high uncertainties. Considering the distribution of the IP, the main weakness hinges on TBT releases to the environment, which is based on an extrapolation from the estimate of emissions in Denmark (DEPA, 1997). Other categories such as inputs of heavy metals also suffer from uncertainties due to low data availability/quality and the lack of comprehensiveness related to the whole EU-15 scale.

Nevertheless, reasoning in terms of orders of magnitude – which is sufficient in the present work – should elude most of those uncertainties. It may also be pointed out that, in spite of those uncertainties, the normalization references from Stranddorf et al. (2005b) are for the time being the best estimates and they are currently widely used in LCA studies.

Influence of uncertainties due to characterization factors

The characterization factors for ecotoxicity in the EDIP97 methodology is based on the Predicted No Effect Concentrations (PNEC), see Chapter 3. Due to the comparative framework of LCA, it is sought to use only PNECs based on results from as standardized laboratory toxicity tests as possible with a population relevant endpoint, see Larsen and Hauschild (2007b) for further details. However, in (tiered) risk assessments (the source of most PNECs, also regarding pharmaceuticals), other endpoints and high assessment factors may be included, leading to lower PNECs than the ones aimed for in LCA. For some pharmaceuticals this is actually the case. In table 10.7 the CFs for these pharmaceuticals are shown in both a version based on rigorous PNECs (RA-based CFs) and the version used in the main assessment in this study (main CFs), as also depicted in Table 10.1.

The effect of substituting the “main assessment” CFs with the rigorous ones (i.e. the RA-based) on the importance of pharmaceuticals regarding the normalization reference for the impact category on chronic aquatic ecotoxicity (ETWC) for EU-15 and Denmark were investigated and the result shown in Table 10.8.

Table 10.7 Risk-assessment (RA)-based characterization factors (CFs) as compared the CFs used in the main assessment for some pharmaceuticals. Impact category: Chronic aquatic ecotoxicity (ETWC).

Pharmaceuticals	CFs used in the main assessment ¹ (m ³ /g)	Rigorous CFs (RA-based) ² (m ³ /g)	Ratio (RA-based CFs/main CFs)
Carbamazephin	4.00E+02	2.00E+03	5.0
Clofibric acid	4.07E+01	2.00E+02	4.9
Diclofenac	1.00E+01	1.00E+04	1000.0
Erythromycin	5.00E+03	5.00E+04	10.0
Ibuprofen	5.21E+00	1.67E+02	32.0
Metoprolol	1.32E+01	1.37E+02	10.4
Sulfamethoxazole	1.69E+03	6.67E+03	3.9

¹ Also shown in Table 1 together with CFs for all included pharmaceuticals

² Larsen and Hansen (2009)

Table 10.8 Impact potentials by substance-category and normalization references (year 1994) for the impact category on chronic aquatic ecotoxicity (ETWC) for Denmark and EU-15, resulting from using RA-based characterization factors for some of the pharmaceuticals¹.

ETWC	Denmark		EU-15	
	IP _{etwc} (m ³ /yr)	% _{etwc}	IP _{etwc} (m ³ /yr)	% _{etwc}
Heavy metals ⁴	7.77E+11	19%	4.16E+13	32%
Organic compounds ⁴	3.75E+11	9%	1.89E+13	15%
Oil	Not included	-	3.63E+12	3%
TBT	2.83E+12	69%	5.38E+13	41%
Atmospheric depositions ²	1.37E+11	3%	1.24E+13	10%
Pharmaceuticals	2.83E+08	0.0069%	1.43E+10	0.011%
TOTAL	4.12E+12	100.0%	1.30E+14	100.0%
Population 1994 ³	5.20E+06		3.70E+08	
Normalization references	7.92E+05	m³/year/capita	3.52E+05	m³/year/capita

¹ All impact potentials, but the one on pharmaceuticals, are extracted from Stranddorf et al. (2005b)

² The category “Atmospheric depositions” refers to airborne emissions of heavy metals, which deposit on aquatic ecosystems.

³ UN (2009) ⁴ Via waste water

The results in Table 10.8 demonstrate that the role of pharmaceuticals is still negligible when introducing rigorous/conservative risk-assessment-based characterization factors; contributions of ca. 0.01% for EU-15 and even less for Denmark are obtained. This is mainly explained by the fact that the most potent compounds are not affected by huge variations between rigorous risk-assessment-based characterization factors and the ones used in the main assessment. Erythromycin represents the worst case, and is actually responsible for most of the change; diclofenac plays also a significant role due to the large increase of its characterization factor.

Thus, this sensitivity analysis shows that even though more rigorous or conservative characterization factors are included (Table 10.7), the contribution of pharmaceuticals still range well below the total potential (i.e. about a factor of 10^4 below).

Combined influence of uncertainties

Combining results from both previously-described sensitivity analyses (Table 10.6 and Table 10.8), a “worst case scenario” can be defined for ETWC regarding EU-15 (most sensitive scenario, i.e. the highest contribution from pharmaceuticals to the total impact potentials is obtained). This case reflects the largest influence from pharmaceuticals to the normalization references since rigorous/conservative characterization factors are used along with the upper range of pharmaceuticals’ consumptions. As shown in Table 10.8, including rigorous characterization factors might induce a contribution of 0.011% to the total impact potential. When combined with the upper range of pharmaceutical consumption it leads to a contribution 15 times higher, i.e. 0.16% to the total impact potential or normalization reference.

Thus, even considering this highly conservative “worst situation” does not make the contribution of the pharmaceuticals rise enough to have a notable influence on the normalization references.

10.2.3 Conclusion

In this study using a conservative approach the observed contribution of pharmaceuticals to the normalization references for ecotoxicity-related impact categories only amounts to a fraction ranging between 3 and 5 orders of magnitude below the total impact potential. Sensitivity analyses including even more conservative emission data or more rigorous characterization factors indicate potential increases of these contributions, but still below 0.1% of the total impact potentials. In a “worst case scenario”, regarding the impact category on chronic aquatic ecotoxicity (EU-15), combining the even more conservative emission data with the rigorous characterization factors results in a contribution from pharmaceuticals to the total impact potential of only about 0.2%.

Thus, this analysis suggests that the ability of the pharmaceuticals to affect EDIP97 normalization references on ecotoxicity is very low and therefore reasonable to be neglected in the normalization inventory. Nevertheless, this result is only valid when assuming that all significant potent chemicals, released in influential amounts, are covered in the inventory, which might not necessarily be the case in the present study. It is therefore recommended to perform a reassessment when a lot more pharmaceuticals and other “new” micropollutants have been attributed characterization factors.

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Database used (electronic):

EMEP/CEIP activity data and emission database – expected to provide officially reported data, gap-filled emissions and activity data on a yearly basis; <http://www.emep-emissions.at/emission-data-webdab>

EUROSTAT database, section Agriculture and environment – expected to contain updated data on consumption of pesticides; <http://epp.eurostat.ec.europa.eu/portal/page/portal/environment/data/database>

EUROSTAT tables, section Population and Social conditions - Population – expected to contain yearly updated data (both national and european);

http://epp.eurostat.ec.europa.eu/portal/page?_pageid=0,1136184,0_45572598&_dad=portal&_schema=PORTAL

EUROSTAT tables, section Economy and Finance – National accounts – expected to contain yearly updated data (both national and european);

http://epp.eurostat.ec.europa.eu/portal/page?_pageid=0,1136184,0_45572598&_dad=portal&_schema=PORTAL

EUROSTAT tables, section Environment and Energy - Water – expected to contain yearly updated data (both national and european);

http://epp.eurostat.ec.europa.eu/portal/page?_pageid=1090,30070682,1090_33076576&_dad=portal&_schema=PORTAL

LCA Center, expected to provide updated characterization factors for EDIP Methodology;

<http://www.lca-center.dk/cms/site.aspx?p=1595>

Appendix I: Equations for EDIP 200X ecotoxicity CFs

The basic structure of the EDIP200X ecotoxicity characterization factor (ECF) is as follow:

$$ECF = f * BIO * EEI = f * DT50/1000 * 0.5/HC50 \quad (31)$$

Below is a summarisation of the fate factors, i.e. the distribution factors and the BIO factor followed by equations for the different ECFs, and a list of definitions

Summarizing constants and fate factors

Constants

Area fractions

$$a = 0.03 \quad (\text{Table 3.5})$$

$$b = 0.25 \quad (\text{Table 3.5})$$

Volume ratios

$$k_{\text{vol-ratio,p-a}} = 2 \cdot 10^{-11} \quad (\text{Section 3.1.2.2})$$

$$k_{\text{vol-ratio,a-fw}} = 333.3 \quad (\text{Section 3.1.2.3})$$

$$k_{\text{vol-ratio,a-s}} = 50,000 \quad (\text{Section 3.1.2.4})$$

$$k_{\text{vol-ratio,a-mw}} = 10 \quad (\text{Section 3.1.2.5})$$

Time

$$t = 1 \text{ day} \quad (\text{Section 3.1.2.2})$$

$$t_{\text{wrt}} = 40 \text{ days} \quad (\text{Section 3.1.2.3})$$

Distribution factors and other fate factors

Direct emissions to air:

$$f_a = 0.5^{(t/DT50_{\text{air}})} \cdot (1 / ((8,420 \cdot k_{\text{vol-ratio,p-a}} \cdot K_{\text{ow}} / H) + 1)) + (1 / (1 + H / (8,420 \cdot k_{\text{vol-ratio,p-a}} \cdot K_{\text{ow}}))) \quad (7)$$

$$f_{\text{sc(via air)}} = f_a \cdot (1 - a - b) \quad (8)$$

$$f_{\text{fwc(via air)}} = f_a \cdot a \quad (9)$$

$$f_{\text{mwc(via air)}} = f_a \cdot b \quad (10)$$

Direct emissions to water:

$$f_{\text{fwa}} = 1 \quad (11)$$

$$f_{a(\text{via freshwater})} = 1/(1 + 1/(k_{\text{vol-ratio,a-fw}} * H/2,480)) \quad (13)$$

$$f_{\text{fwc(via freshwater)}} = 1/((k_{\text{vol-ratio,a-fw}} * H/2,480) + 1) + f_{a(\text{via freshwater})} * f_{\text{fwc(via air)}} \quad (14)$$

$$f_{\text{sc(via freshwater)}} = f_{a(\text{via freshwater})} * f_{\text{sc(via air)}} \quad (15)$$

$$f_{\text{mwc(via freshwater)}} = f_{a(\text{via freshwater})} * f_{\text{mwc(via air)}} + f_{\text{fwc(via freshwater)}} * 0.5^{(t_{\text{wrt}}/DT50_{\text{freshwater}})} \quad (16)$$

Direct emissions to soil:

$$f_{a(\text{via soil})} = (1/(1+1/(k_{\text{vol-ratio,a-s}} * H/2,480))) * 1/(0.09 * K_{\text{oc}} + 1) \quad (21)$$

$$(\text{for inorganics: } 1/(1+1/(k_{\text{vol-ratio,a-s}} * H/2,480)) * 1/(4.5 * K_{\text{d}} + 1)) \quad (21+18))$$

$$f_{\text{sc(via soil)}} = (1/((k_{\text{vol-ratio,a-s}} * H/2,480) + 1)) * (1/(0.09 * K_{\text{oc}} + 1)) * 0.95 + (f_{a(\text{via soil})} * f_{\text{sc(via air)}}) \quad (22)$$

$$(\text{for inorganics: } (1/((k_{\text{vol-ratio,a-s}} * H/2,480) + 1)) * (1/(4.5 * K_{\text{d}} + 1)) * 0.95 + (f_{a(\text{via soil})} * f_{\text{sc(via air)}})) \quad (22+18))$$

$$f_{\text{fwc(via soil)}} = (f_{a(\text{via soil})} * f_{\text{fwc(via air)}}) + (1/((k_{\text{vol-ratio,a-s}} * H/2,480) + 1)) * (1/(0.09 * K_{\text{oc}} + 1)) * 0.05 \quad (23)$$

$$(\text{for inorganics: } (f_{a(\text{via soil})} * f_{\text{fwc(via air)}}) + (1/((k_{\text{vol-ratio,a-s}} * H/2,480) + 1)) * (1/(4.5 * K_{\text{d}} + 1)) * 0.05) \quad (23+18))$$

$$f_{\text{mwc(via soil)}} = f_{a(\text{via soil})} * f_{\text{mwc(via air)}} \quad (24)$$

Direct emissions to marine water:

$$f_{\text{mwa}} = 1 \quad (25)$$

$$f_{a(\text{via marine water})} = 1/(1 + 1/(k_{\text{vol-ratio,a-mw}} * H/2,480)) \quad (26)$$

$$f_{\text{mwc(via marine water)}} = 1/((k_{\text{vol-ratio,a-mw}} * H/2,480) + 1) + (f_{a(\text{via marine water})} * f_{\text{mwc(via air)}}) \quad (27)$$

$$f_{\text{fwc(via marine water)}} = f_{a(\text{via marine water})} * f_{\text{fwc(via air)}} \quad (28)$$

$$f_{\text{sc(via marine water)}} = f_{a(\text{via marine water})} * f_{\text{sc(via air)}} \quad (29)$$

Diverse equations

$$K_{\text{oc(pH=7)}} = K_{\text{oc(non-polar)}} / (1 + 10^{(\text{pH}-\text{pKa})}) = K_{\text{oc(non-polar)}} / (1 + 10^{(7-\text{pKa})}) \quad (20)$$

$$K_{\text{oc}} = 1.26 * K_{\text{ow}}^{0.81} \quad (\text{predominantly hydrophobics}) \quad (\text{Section 3.1.2.4})$$

Ecotoxicity characterization factors (ECFs)

The characterization factors are expressed in PAF*m³ per gram substance emitted if effect data are expressed in mg/L.

Direct emissions to air

$$ECF_{(fwc)a} = f_{fwc(via\ air)} * BIO_{fw} * EEI_{chronic} = f_a * a * (DT50_{fw}/1000) * (0.5/HC50_{chronic}) \quad (32)$$

$$ECF_{(sc)a} = f_{sc(via\ air)} * BIO_s * EEI_{chronic} = f_a * (1-a-b) * (DT50_s/1000) * (0.5/HC50_{chronic}) \quad (33)$$

$$ECF_{(mwc)a} = f_{mwc(via\ air)} * BIO_{mw} * EEI_{chronic} = f_a * b * (DT50_{mw}/1000) * (0.5/HC50_{chronic}) \quad (34)$$

Direct emissions to freshwater

$$ECF_{(fwa)w} = f_{fwa} * 0.5/HC50_{acute} \quad (35)$$

$$ECF_{(fwc)w} = f_{fwc(via\ fw)} * BIO_{fw} * EEI_{chronic} = f_{fwc(via\ fw)} * (DT50_{fw}/1000) * (0.5/HC50_{chronic}) \quad (36)$$

$$ECF_{(sc)w} = f_{sc(via\ fw)} * BIO_s * EEI_{chronic} = f_{a(via\ fw)} * f_{sc(via\ air)} * (DT50_s/1000) * (0.5/HC50_{chronic}) \quad (37)$$

$$ECF_{(mwc)w} = f_{mwc(via\ fw)} * BIO_{mw} * EEI_{chronic} = (f_{a(via\ fw)} * f_{mwc(via\ air)} + f_{fwc(via\ fw)} * 0.5^{(t_{wrt}/DT50_{fw})}) * (DT50_{mw}/1000) * (0.5/HC50_{chronic}) \quad (38)$$

Direct emissions to soil

$$ECF_{(sc)s} = f_{sc(via\ soil)} * BIO_s * EEI_{chronic} = ((1/((k_{vol-ratio,a-s} * H/2,480) + 1)) * (1/(0.09 * K_{oc} + 1))) * 0.95 + (f_{a(via\ soil)} * f_{sc(via\ air)}) * (DT50_s/1000) * (0.5/HC50_{chronic}) \quad (39)$$

$$ECF_{(fwc)s} = f_{fwc(via\ soil)} * BIO_{fw} * EEI_{chronic} = ((f_{a(via\ soil)} * f_{fwc(via\ air)}) + (1/((k_{vol-ratio,a-s} * H/2,480) + 1)) * (1/(0.09 * K_{oc} + 1))) * 0.05 * (DT50_{fw}/1000) * (0.5/HC50_{chronic}) \quad (40)$$

$$ECF_{(mwc)s} = f_{mwc(via\ soil)} * BIO_{mw} * EEI_{chronic} = f_{a(via\ soil)} * f_{mwc(via\ air)} * (DT50_{mw}/1000) * (0.5/HC50_{chronic}) \quad (41)$$

Direct emissions to marine water

$$ECF_{(mwa)mw} = f_{mwa} * 0.5/HC50_{acute} \quad (42)$$

$$ECF_{(mwc)mw} = f_{mwc(via\ marine\ water)} * BIO_{mw} * EEI_{chronic} = (1/((k_{vol-ratio,a-mw} * H/(2,480)) + 1) + (f_{a(via\ marine\ water)} * f_{mwc(via\ air)})) * (DT50_{mw}/1000) * (0.5/HC50_{chronic}) \quad (43)$$

$$ECF_{(fwc)mw} = f_{fwc(via\ marine\ water)} * BIO_{fw} * EEI_{chronic} = f_{a(via\ marine\ water)} * f_{fwc(via\ air)} * (DT50_{fw}/1000) * (0.5/HC50_{chronic}) \quad (44)$$

$$ECF_{(sc)mw} = f_{sc(via\ marine\ water)} * BIO_s * EEI_{chronic} = f_{a(via\ marine\ water)} * f_{sc(via\ air)} * (DT50_s/1000) * (0.5/HC50_{chronic}) \quad (45)$$

Definitions

BIO	Fate factor related to the potential for biodegradation of a given substance
Distribution factor:	Fate factor regarding the fraction of total emitted substance amount that ends up in each defined environmental compartment

Fate factor:	Factor related to the fate in the environment of an emitted substance
f_a	Fate factor regarding persistence in the transient compartment air for a substance directly emitted to air ("distribution factor from air to air")
$f_{sc(via\ air)}$	Distribution factor regarding fraction ending up in soil after emission to air (exhibiting potential chronic effects on biota in soil)
$f_{fwc(via\ air)}$	Distribution factor regarding fraction ending up in freshwater after emission to air (exhibiting potential chronic effects on biota in freshwater)
$f_{mwc(via\ air)}$	Distribution factor regarding fraction ending up in marine water after emission to air (exhibiting potential chronic effects on biota in marine water)
f_{fwa}	Distribution factor regarding fraction (i.e. 1) ending up in freshwater after direct emission to freshwater (exhibiting potential acute effects on biota in freshwater)
$f_{a(via\ freshwater)}$	Distribution factor regarding fraction ending up in the transient compartment air for a substance emitted to freshwater
$f_{fwc(via\ fresh\ water)}$	Distribution factor regarding fraction ending up in freshwater after emission to freshwater (exhibiting potential chronic effects on biota in freshwater)
$f_{sc(via\ freshwater)}$	Distribution factor regarding fraction ending up in soil after emission to freshwater (exhibiting potential chronic effects on biota in soil)
$f_{mwc(via\ freshwater)}$	Distribution factor regarding fraction ending up in marine water after emission to freshwater (exhibiting potential chronic effects on biota in marine water)
$f_{a(via\ soil)}$	Distribution factor regarding fraction ending up in the transient compartment air for a substance emitted to soil
$f_{sc(via\ soil)}$	Distribution factor regarding fraction ending up in soil after emission to soil (exhibiting potential chronic effects on biota in soil)
$f_{fwc(via\ soil)}$	Distribution factor regarding fraction ending up in freshwater after emission to soil (exhibiting potential chronic effects on biota in freshwater)
$f_{mwc(via\ soil)}$	Distribution factor regarding fraction ending up in marine water after emission to soil (exhibiting potential chronic effects on biota in marine water)
f_{mwa}	Distribution factor regarding fraction (i.e. 1) ending up in marine water after direct emission to marine water (exhibiting potential acute effects on biota in marine water)
$f_{mwc(via\ marine\ water)}$	Distribution factor regarding fraction ending up in marine water after emission to marine water (exhibiting potential chronic effects on biota in marine water)

$f_{\text{fwc(via marine water)}}$	Distribution factor regarding fraction ending up in freshwater after emission to marine water (exhibiting potential chronic effects on biota in freshwater)
$f_{\text{sc(via marine water)}}$	Distribution factor regarding fraction ending up in soil after emission to marine water (exhibiting potential chronic effects on biota in soil)

Appendix II: Gross Domestic Products (GDP)

Table II-1 *Gross domestic product at market prices in 2004 (millions of US dollars) ¹*

Country	GDP	Fraction
Albania	7.38E+09	0.1%
Austria	2.94E+11	2.0%
Belarus	2.31E+10	0.2%
Belgium	3.58E+11	2.5%
Bosnia/Herzegovina	9.31E+09	0.1%
Bulgaria	2.46E+10	0.2%
Croatia	3.56E+10	0.2%
Czech Republic	1.08E+11	0.8%
Denmark	2.45E+11	1.7%
Estonia	1.17E+10	0.1%
Finland	1.86E+11	1.3%
France	2.06E+12	14.3%
Germany	2.75E+12	19.1%
Greece	2.09E+11	1.5%
Hungary	1.02E+11	0.7%
Ireland	1.84E+11	1.3%
Italy	1.72E+12	12.0%
Kalingrad region	-	-
Kola Karelia	-	-
Latvia	1.38E+10	0.1%
Lithuania	2.25E+10	0.2%
Luxembourg	3.36E+10	0.2%
Moldova	2.60E+09	0.0%
Netherlands	6.07E+11	4.2%
Norway	2.55E+11	1.8%
Poland	2.53E+11	1.8%
Portugal	1.78E+11	1.2%
Remaining Russia	5.92E+11	4.1%
Romania	7.55E+10	0.5%
Slovakia	4.20E+10	0.3%
Slovenia	3.26E+10	0.2%
Spain	1.04E+12	7.2%
St-Petersburg	-	-
Sweden	3.50E+11	2.4%
Switzerland	3.59E+11	2.5%
Ukraine	6.48E+10	0.5%
United Kingdom	2.13E+12	14.8%
Yugoslavia	5.37E+09	0.0%
Total	1.44E+13	100%

¹ Source: UN (2009)

Appendix III: Coastal GDP

EUROSTAT (2009) defines an inland width of 100 km to calculate the total coastal area by country. However, in the framework of this study, the coastal gross domestic products, which is the keystone of this extrapolation, is supposed to be used for representing direct emissions to seas. Therefore a width of 100 km becomes too large since waste water treatment plants (WWTP) located at such distance from the sea do not discharge directly into the sea.

Thus, a width of 20 km inland was assumed to define “new” coastal areas (e.g. meaning 20% of the area defined by EUROSTAT (2009) for straight coastlines). A correction of the area presented in EUROSTAT (2009) was then applied as illustrated in Table III-2 (application in *column 3* of Table III-1). The shape of the coastlines was also taken into account (roughly) in the correction, based on a subjective judgment.

Combining this correction of the coastal areas and figures from EUROSTAT (2009), coastal GDP were then calculated (cf. *column 8* in Table III-1).

Table III-1 *Definition of the coastal gross domestic products (coastal GDP)*

Coastal countries	Area ¹ (km ²)	Correcting factor ²	Area considered (km ²)	Coastal Population densities ¹ (inhab./km ²)	Coastal population	Coastal GDP ¹ (€/capita)	Coastal GDP (€)
Belgium	6,000	A	1,200	520	624,000	26,500	1.65E+10
Bulgaria	16,000	A	3,200	60	192,000	3,500	6.72E+08
Denmark	40,000	C	12,000	125	1,500,000	40,000	6.00E+10
Estonia	30,000	C	9,000	40	360,000	11,000	3.96E+09
Finland	185,000	B	46,250	30	1,387,500	35,500	4.93E+10
France	250,000	B	62,500	100	6,250,000	24,500	1.53E+11
Germany	40,000	A	8,000	140	1,120,000	23,000	2.58E+10
Greece	110,000	C	33,000	100	3,300,000	19,500	6.44E+10
Ireland	62,000	C	18,600	60	1,116,000	42,500	4.74E+10
Italy	180,000	B	45,000	220	9,900,000	22,000	2.18E+11
Latvia	25,000	B	6,250	60	375,000	9,000	3.38E+09
Lithuania	3,000	A	600	90	54,000	7,500	4.05E+08
Netherlands	25,000	A	5,000	500	2,500,000	35,000	8.75E+10
Norway ³	305,000	A	61,000	40	2,440,000	35,000	8.54E+10
Poland	45,000	A	9,000	100	900,000	7,000	6.30E+09
Portugal	35,000	A	7,000	225	1,575,000	15,500	2.44E+10
Romania	16,000	A	3,200	80	256,000	5,000	1.28E+09
Slovenia	3,000	A	600	50	30,000	14,500	4.35E+08
Spain	155,000	A	31,000	160	4,960,000	22,000	1.09E+11
Sweden	305,000	B	76,250	40	3,050,000	35,500	1.08E+11
United Kingdom ⁴	200,000	C	60,000	320	19,200,000	32,500	6.24E+11

¹ EUROSTAT (2009)

² Attribution of the correcting factor is entirely subjective (author's assessment), see Table III-2

³ Norway was not reported but it was assumed identical to Sweden

⁴ A probable mistake in the figure 4 of EUROSTAT (2009), depicting an area for UK of "15,000 km²" was identified and corrected to 200,000 km², estimated from the figure 1 (in EUROSTAT 2009) and from the total area of UK (245,000 km²).

Table III-2 *Correction factors to get a 20 km-inland width in the considered area*¹

Correction factor	Notes	Designation
20%	countries with straight coastlines	A
25%	countries with few curves	B
30%	countries with many curves	C

¹ The definition of the correcting factors is subjective and is based on the aim of outlining a 20 km inland width, i.e. 20% of the considered width in EUROSTAT (2009). The topography was included, following this principle: the more the coastline is curved the less the area is decreased when reducing the considered width from 100 km to 20 km.

Appendix IV: Emission data for heavy metals

Table IV-1 *Reported and extrapolated emissions of heavy metals allocated to the freshwater environment (i.e. freshwater compartment) in Europe (point 1 in Figure 3.1 in Chapter 3)*

2004	Cd (t)	Hg (t)	Pb (t)	Cu (t)	Zn (t)
Albania	0.16	0.06	1.51	6.67	23.62
Austria	6.23	2.40	60.41	266.03	941.86
Belarus	0.49	0.19	4.75	20.92	74.06
Belgium	4.75	0.80	100.41	224.00	2156.00
Bosnia/Herzegovina	0.20	0.08	1.91	8.41	29.78
Bulgaria	0.52	0.20	5.06	22.28	78.88
Croatia	0.75	0.29	7.31	32.20	113.99
Czech Republic	2.29	0.88	22.21	97.81	346.30
Denmark	0.40	0.15	11.18	279.46	646.60
Estonia	0.92	14.15	8.21	84.00	132.00
Finland	2.60	1.02	34.48	744.00	3448.00
France	45.79	6.06	96.93	406.08	2384.05
Germany	6.28	7.64	197.33	660.00	3740.00
Greece	4.43	1.71	42.92	189.01	669.19
Hungary	2.16	0.83	20.97	92.34	326.93
Ireland	6.10	27.60	74.50	267.20	899.64
Italy	36.51	14.07	353.93	1558.73	5518.58
Kalingrad region					
Kola Karelia					
Latvia	1.39	0.00	23.68	168.00	592.00
Lithuania	0.01	3.28	17.73	84.00	552.00
Luxembourg	0.71	0.27	6.89	30.36	107.50
Moldova	0.06	0.02	0.53	2.35	8.31
Netherlands	7.60	5.76	232.92	939.60	3409.20
Norway	4.55	2.00	62.47	1068.00	2396.00
Poland	1.30	4.51	39.32	368.00	2780.00
Portugal	0.40	0.07	7.07	48.00	248.00
Remaining Russia	32.93	0.00	363.76	1528.00	384.00
Romania	1.60	0.62	15.49	68.23	241.58
Slovakia	0.89	0.34	8.62	37.98	134.46
Slovenia	0.69	0.27	6.69	29.47	104.33
Spain	109.52	12.00	438.41	796.00	2568.00
St-Petersburg					
Sweden	2.17	0.69	58.56	1015.20	3408.00
Switzerland	7.59	2.93	73.60	324.15	1147.62
Ukraine	1.37	0.53	13.31	58.60	207.46
United Kingdom	11.22	6.00	539.38	1477.60	6217.20
Yugoslavia	0.11	0.04	1.10	4.85	17.18
Total Europe	304.68	117.45	2,953.56	13,007.55	46,052.34

Table VI-2 Reported and extrapolated riverine inputs of heavy metals to marine water environment (i.e. marine water compartment) in Europe (point 2 in Figure 3.1 in Chapter 3)

2004	Cd (t)	Hg (t)	Pb (t)	Cu (t)	Zn (t)
Albania	0.12	0.02	1.07	1.67	5.90
Austria	4.72	0.60	42.71	66.51	235.46
Belarus	0.37	0.05	3.36	5.23	18.51
Belgium	3.60	0.20	71.00	56.00	539.00
Bosnia/Herzegovina	0.15	0.02	1.35	2.10	7.45
Bulgaria	0.40	0.05	3.58	5.57	19.72
Croatia	0.57	0.07	5.17	8.05	28.50
Czech Republic	1.74	0.22	15.70	24.45	86.58
Denmark	0.30	0.04	7.90	69.87	161.65
Estonia	0.70	3.54	5.80	21.00	33.00
Finland	1.97	0.26	24.38	186.00	862.00
France	34.70	1.51	68.54	101.52	596.01
Germany	4.76	1.91	139.53	165.00	935.00
Greece	3.36	0.43	30.35	47.25	167.30
Hungary	1.64	0.21	14.83	23.09	81.73
Ireland	4.62	6.90	52.68	66.80	224.91
Italy	27.67	3.52	250.27	389.68	1,379.64
Kalingrad region					
Kola Karelia					
Latvia	1.05	0.00	16.74	42.00	148.00
Lithuania	0.01	0.82	12.54	21.00	138.00
Luxembourg	0.54	0.07	4.88	7.59	26.88
Moldova	0.04	0.01	0.38	0.59	2.08
Netherlands	5.76	1.44	164.70	234.90	852.30
Norway	3.45	0.50	44.17	267.00	599.00
Poland	0.98	1.13	27.81	92.00	695.00
Portugal	0.30	0.02	5.00	12.00	62.00
Remaining Russia	24.95	0.00	257.21	382.00	96.00
Romania	1.21	0.15	10.96	17.06	60.40
Slovakia	0.67	0.09	6.10	9.49	33.62
Slovenia	0.52	0.07	4.73	7.37	26.08
Spain	83.00	3.00	310.00	199.00	642.00
St-Petersburg					
Sweden	1.64	0.17	41.41	253.80	852.00
Switzerland	5.75	0.73	52.04	81.04	286.91
Ukraine	1.04	0.13	9.41	14.65	51.87
United Kingdom	8.50	1.50	381.40	369.40	1,554.30
Yugoslavia	0.09	0.01	0.78	1.21	4.30
Total Europe	230.90	29.36	2,088.48	3,251.89	11,513.08

Table VI-3 Reported and extrapolated direct discharges of heavy metals to marine water environment (i.e. marine water compartment) in Europe (point 2 in Figure 3.1 in Chapter 3)

2004	Cd (t)	Hg (t)	Pb (t)	Cu (t)	Zn (t)
Albania					
Austria					
Belarus					
Belgium	0.00	0.00	0.00	0.00	0.00
Bosnia/Herzegovina					
Bulgaria	0.00	0.00	0.03	0.08	0.33
Croatia					
Czech Republic					
Denmark ³	0.09	0.03	2.67	6.83	29.53
Estonia	0.26	0.32	0.28	1.80	3.40
Finland	0.06	0.01	0.06	0.70	7.60
France	0.24	0.08	6.82	17.44	75.37
Germany	0.08	0.05	1.50	3.20	16.00
Greece	0.10	0.03	2.87	7.33	31.68
Hungary					
Ireland	0.09	0.00	8.09	11.53	92.20
Italy	0.34	0.12	9.70	24.81	107.21
Kalingrad region					
Kola Karelia					
Latvia	0.07	0.00	1.26	1.90	5.70
Lithuania	0.00	0.00	0.00	0.20	1.50
Luxembourg					
Moldova					
Netherlands	0.17	0.02	2.50	3.60	30.00
Norway	0.09	0.15	2.22	18.00	23.00
Poland	0.09	0.00	0.60	0.20	2.00
Portugal ⁴	0.04	0.01	1.09	2.78	12.02
Remaining Russia	0.15	0.01	1.79	3.80	41.00
Romania	0.00	0.00	0.06	0.15	0.63
Slovakia					
Slovenia	0.00	0.00	0.02	0.05	0.21
Spain	9.20	1.70	46.00	19.00	45.00
St-Petersburg					
Sweden	0.25	0.05	1.99	12.58	61.90
Switzerland					
Ukraine					
United Kingdom	0.73	0.27	28.00	66.30	270.90
Yugoslavia					
Total Europe	12.04	2.87	117.54	202.28	857.19

Appendix V: Emission data for oil compounds

Speciation for oil spills is highly dependent on the type of oil and large variations occur when considering oil from different geographical areas (Fingas and Fieldhouse 2004). However, in order to assess the influence of oil spills on the normalization references (and de facto to provide a first estimate of this contribution), it was attempted to draw an average speciation of crude oil.

A global average profile has been defined:

Table V-1 Average speciation for crude oil ¹

	Distribution
Saturates	51.79%
Aromatics	28.77%
Resins	12.14%
Asphaltenes	7.30%
Subtotal {Saturates + Aromatics}	80.56%

¹ Based on Fingas and Fieldhouse (2004)

For data availability reasons, resins and asphaltenes were not assessed and the focus was laid only on saturates and aromatics.

To draw a profile for saturates and aromatics, the *Total Petroleum Hydrocarbon Criteria Work Group* (Potter and Simmons 1998) reports in its *Volume 2* a summary of composition data for crude oil (only aromatics and saturates). However, this composition corresponds to a speciation of 27% of the total weight (*column 2* in Table V-2), and not 80.56% as required in Table V-1. It was then assumed that each compound reported by Potter and Simmons (1998) is representative of the chemical class which it belongs to (*column 1* in Table V-2). That point allowed to extrapolate and bring up the reported speciation to represent 80.56% of the total weight, with respect to saturates and aromatics' distribution defined by Fingas and Fieldhouse (2004) (*column 3* in Table V-2).

Potter and Simmons (1998) also provides maximum range weight (%) for some compounds composing crude oil (*column 4* in Table V-2). Those weight percentages can be directly compared with the one used in the assessment (*column 3*). Overall, used weights outnumber the maximum range. However, the effect of this overestimation on the final impact potential from oil spills has to be considered with respect to the distribution of this potential among the different assessed compounds (those for which characterization factors are available; see *column 5*).

Table V-2 Crude oil average speciation profile (incl. only saturates and aromatics)

Compounds	Raw ¹ wt%	Adapted ² wt%	Max reported ¹ wt%	Assess. ³
Alkyl-monoaromatics	3.819%	16.359%		
Benzene	0.160%	0.685%	0.410%	x
Toluene	0.670%	2.870%	2.500%	x
1,2 di-ethylbenzene	0.024%	0.103%		x
ethylbenzene	0.170%	0.728%	0.310%	x
m+p xylene	0.500%	2.142%	0.800%	
m xylene	0.660%	2.827%	2.000%	x
o xylene	0.260%	1.114%	0.680%	x
p xylene	0.260%	1.114%	0.680%	x
1,2,3-trimethylbenzene	0.100%	0.428%		x
1,2,4-trimethylbenzene	0.240%	1.028%	0.510%	x
1,3,5-trimethylbenzene	0.180%	0.771%	0.690%	x
1-methyl-2-ethylbenzene	0.050%	0.214%	0.090%	
1-methyl-3-ethylbenzene	0.140%	0.600%	0.400%	
1-methyl-4-ethylbenzene	0.060%	0.257%		
isopropylbenzene	0.044%	0.188%	0.090%	x
n-propylbenzene	0.086%	0.368%	0.260%	x
1,2,3,5-tetramethylbenzene	0.027%	0.116%		
1,2,4,5-tetramethylbenzene	0.038%	0.163%		x
1,2-dimethyl-4-ethylbenzene	0.024%	0.103%		
1,3-dimethyl-5-ethylbenzene	0.027%	0.116%		
1-methyl-4-isopropylbenzene	0.012%	0.051%		
indane	0.067%	0.287%		
sec-butylbenzene	0.014%	0.060%		
tert-butylbenzene	0.006%	0.027%	0.010%	x
Branched alkanes	4.227%	11.017%		
2,2-dimethylbutane	0.042%	0.109%	0.043%	
2,3-dimethylbutane	0.110%	0.287%	0.140%	
2-methylpentane	0.370%	0.964%	0.400%	
3-methylpentane	0.360%	0.938%	0.420%	
2,3-dimethylpentane	0.350%	0.912%	0.600%	
2,4-dimethylpentane	0.049%	0.128%		
2-methylhexane	0.700%	1.824%		
3-ethylpentane	0.050%	0.130%		
3-methylhexane	0.340%	0.886%	0.500%	
2,2,3-trimethylpentane	0.004%	0.010%		
2,2-dimethylhexane	0.064%	0.167%	0.120%	
2,3,3-trimethylpentane	0.006%	0.016%		
2,3,4-trimethylpentane	0.005%	0.013%		
2,3-dimethylhexane	0.110%	0.287%	0.160%	
2,4-dimethylhexane	0.060%	0.156%		

Compounds	Raw ¹ wt%	Adapted ² wt%	Max reported ¹ wt%	Assess. ³
2,5-dimethylhexane	0.077%	0.201%	0.095%	
2-methyl-3-heptane	0.040%	0.104%		
3,3-dimethylhexane	0.030%	0.078%		
ethylcyclohexane	0.200%	0.521%		x
2,3-dimethylheptane	0.050%	0.130%		
2,6-dimethylheptane	0.150%	0.391%	0.250%	
2-methyloctane	0.400%	1.043%		
3-methyloctane	0.250%	0.652%	0.420%	
4-methyloctane	0.100%	0.261%		
pristane	0.210%	0.547%		
phytane	0.100%	0.261%		
Cycloalkanes	3.858%	10.055%		
cyclopentane	0.048%	0.125%	0.050%	x
cyclohexane	0.700%	1.824%		x
methylcyclopentane	0.600%	1.564%	0.900%	
1,1-dimethylcyclopentane	0.130%	0.339%	0.200%	
cis-1,3-dimethylcyclopentane	0.200%	0.521%		
ethylcyclopentane	0.190%	0.495%	0.200%	
trans-1,2-dimethylcyclopentane	0.330%	0.860%	0.500%	
trans-1,3-dimethylcyclopentane	0.570%	1.486%	0.900%	
1,1,2-trimethylcyclopentane	0.060%	0.156%		
1,1,3-trimethylcyclopentane	0.250%	0.652%	0.300%	
trans-1,2-cis-4-trimethylcyclopentane	0.330%	0.860%	0.360%	
trans-1,2-dimethylcyclohexane	0.250%	0.652%		x
trans-1,2,4-trimethylcyclohexane	0.200%	0.521%	0.200%	
Diaromatics (except naphtalene)	0.060%	0.257%		
biphenyl	0.040%	0.171%		x
fluorene	0.020%	0.086%	0.060%	x
Monoaromatics	0.090%	0.386%		
tetralin	0.090%	0.386%		x
n-alkanes	11.786%	30.718%		
n-hexane	1.300%	3.388%	1.800%	x
n-heptane	1.600%	4.170%	2.300%	x
n-octane	1.100%	2.867%	1.900%	x
n-nonane	0.940%	2.450%	1.800%	
n-decane	1.100%	2.867%	1.800%	x
n-undecane	1.100%	2.867%	1.700%	
n-dodecane	1.100%	2.867%	1.700%	
n-tridecane	0.450%	1.173%		
n-tetradecane	0.420%	1.095%		
n-pentadecane	0.400%	1.043%		
n-hexadecane	0.370%	0.964%		
n-heptadecane	0.340%	0.886%		
n-octadecane	0.250%	0.652%		

Compounds	Raw ¹ wt%	Adapted ² wt%	Max reported ¹ wt%	Assess. ³
n-nonadecane	0.300%	0.782%		
n-eicosane	0.190%	0.495%		
n-heneicosane	0.160%	0.417%		
n-docosane	0.190%	0.495%		
n-tricosane	0.170%	0.443%		
n-tetracosane	0.130%	0.339%		
n-pentacosane	0.100%	0.261%		
n-hexacosane	0.076%	0.198%		
Naphtalene	2.551%	10.927%		
naphtalene	0.069%	0.296%	0.092%	x
1-mehylnaphtalene	0.130%	0.557%	0.310%	
2-mehylnaphtalene	0.260%	1.114%	0.650%	x
5-methyltetralin	0.080%	0.343%		
6-methyltetralin	0.090%	0.386%		
1,2-dimethylnaphtalene	0.037%	0.158%	0.074%	
1,3- & 1,6-dimethylnaphtalene	0.080%	0.343%		
1,3-dimethylnaphtalene	0.110%	0.471%	0.210%	
1,4- & 2,3- & 1,5-dimethylnaphtalene	0.080%	0.343%		x
1,4-dimethylnaphtalene	0.024%	0.103%	0.068%	
1,5-dimethylnaphtalene	0.036%	0.154%	0.082%	x
1,6-dimethylnaphtalene	0.300%	1.285%	0.570%	
1,7-dimethylnaphtalene	0.110%	0.471%	0.210%	
1&2-ethylnaphtalene	0.048%	0.206%		
1-ethylnaphtalene	0.034%	0.146%	0.085%	
2,3-dimethylnaphtalene	0.076%	0.326%	0.150%	
2,6 & 2,7-dimethylnaphtalene	0.069%	0.296%		x
2,6 -dimethylnaphtalene	0.120%	0.514%	0.230%	x
2,7 -dimethylnaphtalene	0.140%	0.600%	0.280%	
2-ethylnaphtalene	0.066%	0.283%	0.140%	
1,2,4-trimethylnaphtalene	0.030%	0.129%	0.056%	
1,2,5-trimethylnaphtalene	0.047%	0.201%	0.082%	
1,2,6-trimethylnaphtalene	0.042%	0.180%	0.077%	
1,2,7-trimethylnaphtalene	0.055%	0.236%	0.095%	
1,3,5-trimethylnaphtalene	0.026%	0.111%	0.049%	
1,3,6-trimethylnaphtalene	0.100%	0.428%	0.180%	
1,3,7-trimethylnaphtalene	0.067%	0.287%	0.120%	
1,4,6- & 1,3,5-trimethylnaphtalene	0.069%	0.296%	0.099%	
1,4,6-trimethylnaphtalene	0.053%	0.227%	0.095%	
1,6,7-trimethylnaphtalene	0.054%	0.231%	0.096%	
2,3,6-trimethylnaphtalene	0.049%	0.210%	0.089%	
Polynuclear aromatics	0.196%	0.841%		
acenaphthene	0.006%	0.024%		x
acenaphthylene	0.001%	0.006%		
2-methylfluorene	0.015%	0.064%		

Compounds	Raw ¹ wt%	Adapted ² wt%	Max reported ¹ wt%	Assess. ³
anthracene	0.001%	0.005%		x
phenanthrene	0.024%	0.103%	0.059%	x
1-methylphenanthrene	0.013%	0.056%	0.033%	
2-methylphenanthrene	0.017%	0.073%	0.043%	
3-methylphenanthrene	0.016%	0.069%	0.037%	
9-methylphenanthrene	0.015%	0.064%	0.036%	
1,6-dimethylphenanthrene	0.009%	0.038%	0.010%	
1,7-dimethylphenanthrene	0.006%	0.027%	0.012%	
1,8-dimethylphenanthrene	0.001%	0.005%	0.003%	
1,9-dimethylphenanthrene	0.003%	0.014%	0.007%	
2,3-dimethylphenanthrene	0.003%	0.013%	0.006%	
2,6-dimethylphenanthrene	0.008%	0.033%	0.014%	
2,7-dimethylphenanthrene	0.003%	0.014%	0.006%	
2,9-dimethylphenanthrene	0.008%	0.033%	0.009%	
3,6-dimethylphenanthrene	0.008%	0.033%	0.011%	
3,9-dimethylphenanthrene	0.009%	0.037%	0.010%	
9-ethylphenanthrene	0.004%	0.018%	0.007%	
fluoranthene	0.000%	0.002%	0.001%	x
pyrene	0.001%	0.003%	0.002%	x
1-methylpyrene	0.003%	0.011%	0.004%	
4-methylpyrene	0.001%	0.003%		
benz(a)anthracene	0.000%	0.001%	0.001%	x
benzo(g,h,i)fluoranthene	0.000%	0.000%		
chrysene	0.001%	0.006%	0.002%	
chrysene & triphenylene	0.004%	0.016%	0.004%	
triphenylene	0.001%	0.003%	0.001%	
2-methylchrysene	0.003%	0.011%		
3-methylchrysene	0.004%	0.019%		
4- & 6-methylchrysene	0.002%	0.006%		
Benzo(a)pyrene	0.000%	0.001%	0.000%	x
Benzo(b)fluoranthene	0.000%	0.002%		
Benzo(e)pyrene	0.001%	0.004%	0.003%	
benzo(k)fluoranthene	0.002%	0.006%		
perylene	0.004%	0.015%		
2-methylcholanthrene	0.000%	0.001%		
benzo(g,h,i)perylene	0.000%	0.001%	0.001%	
indeno(1,2,3-cd)pyrene	0.001%	0.003%		
coronene	0.000%	0.000%		
TOTAL	26.6%	80.56%		

¹ Total Petroleum Hydrocarbon Criteria Work Group (Potter and Simmons 1998)

² Fingas and Fieldhouse (2004)

³ Compounds marked with a cross were assessed using EDIP 200X characterization factors.

Appendix VI: Emission data for TBT compounds

Table VI-1 Marine area included for European assessment (based on Table 3.4 in Chapter 3)

	Total area (km ²)	Proposed European area (km ²)
Baltic Sea ¹	377 000	377 000
Black Sea	422 000	211 000
English Channel	75 000	75 000
Irish Sea	100 000	100 000
Mediterranean Sea ¹	2 500 000	1 250 000
North Sea	745 750	745 750
Atlantic Ocean ²		300 000
Total		3 058 750

¹ Half of the Baltic Sea and the Mediterranean Sea are included, based on geographical estimates.

² For Atlantic Ocean, only coastal areas are considered, assuming a length of 5 000 km (from Gibraltar to Nordkapp) and a width of 60 km (defined as the coastal zone relevant for commercial fishery, i.e. 80% of fish consumed are caught in this zone).

Table VI-2 Impact potentials (IPs) of organotin compounds for acute ecotoxicity in aquatic environments for Europe ¹

ETWA	Organotin emissions		CF _{etwa} ⁴ (m ³ /kg)	Denmark	Europe
	DK (t/yr) ²	Europe (t/yr) ³		IP _{etwa} (m ³ /yr)	IP _{etwa} (m ³ /yr)
Low	0.6	42.7	1.28E+05	7.67E+07	5.45E+09
High	4.9	348.6	1.28E+05	6.26E+08	4.45E+10
Average				3.51E+08	2.50E+10

¹ Applied only for marine environment

² Estimates from DEPA (1997) (taken from Stranddorf et al. 2005b)

³ Extrapolation based on the area of marine water: an area of 43 000 km² is considered for Denmark, extended to 3 058 750 km² for total Europe (cf. Table VI-1).

⁴ Characterization factor for tributyltin fluoride (TBTF) mass corrected to consider only tributyltin (TBT).

Table VI-3 Impact potentials (IPs) of organotin compounds for chronic ecotoxicity in marine environments for Europe ¹

ETMWC	Organotin emissions		CF _{etmwc} ⁴ (m ³ /kg)	Denmark	Europe
	DK (t/yr) ²	Europe (t/yr) ³		IP _{etmwc} (m ³ /yr)	IP _{etmwc} (m ³ /yr)
Low	0.6	42.7	2.39E+02	1.44E+05	1.02E+07
High	4.9	348.6	2.39E+02	1.17E+06	8.34E+07
Average				6.58E+05	4.68E+07

¹ Applied only for marine environment

² Estimates from DEPA (1997) (taken from Stranddorf et al. 2005b)

³ Extrapolation based on the area of marine water: an area of 43 000 km² is considered for Denmark, extended to 3 058 750 km² for total Europe (cf. Table VI-1).

⁴ Characterization factor for tributyltin fluoride (TBTF) mass corrected to consider only tributyltin (TBT).

Appendix VII: Emission data:atmospheric deposition

Table VII-1a Air emissions of heavy metals for European countries in 2004 ¹

Emissions (ton/yr)	As	Cd	Cr	Cu	Hg
Albania	0.14	0.20	0.31	1.85	0.20
Austria	5.66	1.03	12.39	73.96	0.94
Belarus	1.06	1.84	7.03	9.25	0.63
Belgium	3.09	2.27	19.24	22.63	2.93
Bosnia/Herzegovina	0.18	1.60	0.39	2.34	1.90
Bulgaria	0.47	15.34	1.04	6.19	4.66
Croatia	0.69	0.88	1.50	8.95	0.71
Czech Republic	5.81	2.37	15.76	18.55	2.09
Denmark	0.65	0.62	1.20	9.10	1.12
Estonia	9.79	0.59	9.03	3.83	0.54
Finland	3.77	1.49	23.87	44.58	0.74
France	11.42	6.71	39.56	167.98	8.58
Germany	4.68	2.66	30.48	2078.09	2.82
Greece	4.02	3.00	8.80	52.55	13.00
Hungary	6.25	2.72	7.40	20.04	3.78
Ireland	2.31	0.58	3.88	12.60	0.41
Italy	42.07	7.89	51.82	48.43	10.34
Kalingrad region	-	-	-	-	-
Kola Karelia	-	-	-	-	-
Latvia	0.49	0.46	5.96	2.08	0.03
Lithuania	0.25	0.52	1.57	3.08	0.42
Luxembourg	0.65	0.05	1.41	8.44	0.29
Moldova	0.52	0.11	0.85	1.32	0.32
Netherlands	1.49	1.76	3.13	82.67	1.02
Norway	1.40	0.60	2.96	20.55	0.71
Poland	4.86	44.91	10.64	63.49	19.82
Portugal	3.02	5.34	10.39	18.21	3.06
Remaining Russia	11.38	55.40	24.91	148.70	11.90
Romania	1.45	9.40	3.18	18.97	10.00
Slovakia	16.63	3.60	6.14	32.23	3.17
Slovenia	0.63	1.15	1.37	8.19	0.65
Spain	17.92	18.40	40.50	296.82	11.90
St-Petersburg	-	-	-	-	-
Sweden	8.29	0.52	8.29	52.49	0.79
Switzerland	6.90	1.12	15.10	90.12	1.06
Ukraine	84.36	3.09	196.72	119.37	6.59
United Kingdom	14.39	3.64	38.72	67.23	6.52
Yugoslavia	0.10	9.70	0.23	1.35	1.80
Total	276.78	211.57	605.76	3616.24	135.44

¹ Officially reported emission data are from the EMEP/CEIP-database (white background). For Cd and Hg, gaps have been filled using estimates from Ilyin et al. (2008) (in light grey background). For As, Cr, Cu, gaps have been filled using extrapolations by GDP (in darker grey background).

Table VII-1b Air emissions of heavy metals and dioxins for European countries in 2004 ¹

Emissions (ton/yr)	Ni	Pb	Se	Zn	Dioxins (g-I TEQ)
Albania	0.78	28.00	0.15	3.59	44.00
Austria	31.07	13.07	5.97	143.15	42.75
Belarus	72.97	44.88	0.00	238.52	37.15
Belgium	84.44	80.98	17.97	208.55	64.96
Bosnia/Herzegovina	0.98	72.00	0.19	4.53	59.00
Bulgaria	2.60	143.39	0.50	11.99	239.27
Croatia	3.76	16.00	0.72	17.33	93.00
Czech Republic	16.54	36.65	9.82	169.07	187.33
Denmark	9.46	5.30	1.84	24.16	23.87
Estonia	6.75	37.98	0.01	51.01	3.73
Finland	44.81	27.78	0.00	128.36	31.99
France	168.84	142.26	14.54	267.25	298.79
Germany	108.22	105.90	3.81	1859.06	83.18
Greece	22.07	470.00	4.24	101.71	183.00
Hungary	23.43	33.54	1.29	83.36	73.66
Ireland	26.89	16.39	2.20	18.16	27.32
Italy	164.01	256.13	12.56	864.91	289.50
Kalingrad region	-	-	-	-	-
Kola Karelia	-	-	-	-	-
Latvia	1.59	13.41	0.64	16.56	13.12
Lithuania	13.40	5.23	0.07	67.49	10.80
Luxembourg	3.55	1.90	0.68	16.34	1.60
Moldova	1.42	2.28	0.11	7.86	5.16
Netherlands	13.73	42.67	1.08	101.10	27.85
Norway	0.00	9.96	0.00	0.00	32.30
Poland	26.67	544.26	5.13	122.90	387.00
Portugal	71.66	173.02	23.49	47.48	10.60
Remaining Russia	62.46	330.00	12.01	287.82	716.00
Romania	7.97	241.00	1.53	36.72	249.00
Slovakia	23.41	69.66	7.76	62.04	65.33
Slovenia	3.44	17.29	0.66	15.86	9.15
Spain	275.26	266.80	103.13	728.71	153.41
St-Petersburg	-	-	-	-	-
Sweden	21.19	17.65	0.70	132.64	36.14
Switzerland	37.85	25.23	7.28	174.43	16.19
Ukraine	86.77	194.88	4.96	472.09	1029.00
United Kingdom	80.46	133.77	46.86	512.15	226.64
Yugoslavia	0.57	70.00	0.11	2.61	163.00
Total	1519.02	3689.25	292.00	6999.50	4934.79

¹ Officially reported emission data are from EMEP/CEIP-database (white background). For Pb and Dioxins, gaps have been filled using estimates from Ilyin et al. (2008) and Gusev et al. (2008), respectively (in light grey background). For Ni, Se, Zn, gaps have been filled using extrapolations by GDP (in darker grey background).

Table VII-1c Air emissions of HCB, PCBs and PAHs for European countries in 2004 ¹

Emissions	HCB (kg)	PCBs (kg)	PAHeq (teq)
Albania	55.00	3.26	8.70
Austria	43.86	-	9.10
Belarus	0.59	9.80	37.10
Belgium	36.03	157.93	77.10
Bosnia/Herzegovina	50.00	4.11	16.10
Bulgaria	21.20	270.45	42.92
Croatia	0.00	15.73	9.10
Czech Republic	4.26	88.13	24.38
Denmark	115.00	-	11.75
Estonia	0.16	52.39	13.86
Finland	30.60	180.44	16.50
France	23.93	27.46	26.64
Germany	2.01	17.36	32.15
Greece	175.00	92.33	23.90
Hungary	4.41	-	21.29
Ireland	0.05	81.44	10.55
Italy	0.02	0.25	132.00
Kaliningrad region	-	-	-
Kola Karelia	-	-	-
Latvia	0.45	5.18	33.95
Lithuania	176.00	23.80	15.43
Luxembourg	1.50	14.83	1.47
Moldova	10.00	258.04	3.68
Netherlands	92.00	-	154.28
Norway	1.00	112.46	14.20
Poland	8.11	2255.60	158.15
Portugal	145.00	1154.58	10.60
Remaining Russia	9846.00	261.26	65.00
Romania	2.00	33.33	52.20
Slovakia	2.06	31.69	15.75
Slovenia	0.32	82.52	10.25
Spain	7728.27	0.00	83.49
St-Petersburg	-	-	-
Sweden	0.02	0.10	15.20
Switzerland	56.00	0.00	1.09
Ukraine	2095.00	28.62	248.00
United Kingdom	849.63	1088.17	11.89
Yugoslavia	30.00	2.37	4.09
Total	21605.50	6353.61	1411.87

¹ Officially reported emission data are from EMEP/CEIP (white background). For HCBs, gaps have been filled using estimates from Gusev et al. (2008) (in light grey background). For PCBs, gaps have been filled using extrapolations by GDP (in darker grey background). PAHs were expressed as benzo(a)pyrene equivalent (see details in Table VII-2).

Table VII-2 Methodology to convert Σ PAH into PAH-eqv. (i.e. benzo(a)pyrene) for European countries

	Emissions (t/yr)						Emitted PAH-eq (t)	Conv. factor F ³
	PAH ¹	BaP ²	BbF ²	BkF ²	Indeno ²	Total 4 PAH		
<i>Albania</i>	8.70	2.50	3.30	1.10	1.80	8.70	8.700	0.287
<i>Austria</i>	8.99	2.70	3.30	1.10	2.00	9.10	9.100	0.297
<i>Belarus</i>	37.10	9.09	18.07	4.91	5.04	37.10	37.105	0.245
<i>Belgium</i>	232.76	5.80	5.50	1.70	4.50	17.50	66.401	-
<i>Bosnia/Herzegovina</i>	16.10	4.10	5.50	2.30	4.20	16.10	16.100	0.255
<i>Bulgaria</i>	129.57	6.60	7.20	2.80	4.60	21.20	36.962	-
<i>Croatia</i>	9.10	2.60	3.40	1.20	1.90	9.10	9.100	0.286
<i>Czech Republic</i>	24.38	8.13	7.23	3.26	5.76	24.38	24.377	0.333
<i>Denmark</i>	11.75	3.44	3.75	2.08	2.48	11.75	11.749	0.292
<i>Estonia</i>	13.86	4.15	4.66	2.48	2.57	13.86	13.856	0.299
<i>Finland</i>	16.72	5.00	6.00	2.00	3.50	16.50	16.500	0.303
<i>France</i>	26.64	7.37	8.65	5.94	4.67	26.64	26.643	0.277
<i>Germany</i>	97.06	35.15	39.00	13.00	27.00	114.15	27.688	-
<i>Greece</i>	23.90	6.90	9.00	3.00	5.00	23.90	23.900	0.289
<i>Hungary</i>	21.29	6.52	7.07	3.67	4.03	21.29	21.292	0.306
<i>Ireland</i>	10.55	2.93	3.85	1.98	1.79	10.55	10.548	0.277
<i>Italy</i>	134.09	40.00	48.00	16.00	28.00	132.00	132.000	0.303
<i>Kalingrad reg.</i>	-	-	-	-	-	-	-	-
<i>Kola Karelia</i>	-	-	-	-	-	-	-	-
<i>Latvia</i>	33.95	12.51	16.27	3.65	1.52	33.95	33.954	0.369
<i>Lithuania</i>	15.43	3.65	4.08	2.38	5.32	15.43	15.432	0.236
<i>Luxembourg</i>	1.47	0.44	0.57	0.08	0.38	1.47	1.470	0.299
<i>Moldova</i>	3.68	0.82	1.01	0.40	1.45	3.68	3.682	0.222
<i>Netherlands</i>	465.77	4.90	4.70	1.80	3.40	14.80	132.872	-
<i>Norway</i>	14.21	2.00	5.80	5.30	1.10	14.20	14.200	0.141
<i>Poland</i>	158.15	46.20	49.01	15.33	47.61	158.15	158.147	0.292
<i>Portugal</i>	10.75	3.10	4.00	1.30	2.20	10.60	10.600	0.292
<i>Remain. Russia</i>	65.00	18.00	21.00	12.00	14.00	65.00	65.000	0.277
<i>Romania</i>	52.20	17.00	17.00	7.20	11.00	52.20	52.200	0.326
<i>Slovakia</i>	15.75	4.71	5.41	2.39	3.24	15.75	15.754	0.299
<i>Slovenia</i>	10.25	2.90	3.90	1.40	2.06	10.25	10.253	0.283
<i>Spain</i>	252.04	23.00	30.00	12.00	17.00	82.00	71.901	-
<i>St-Petersburg</i>	-	-	-	-	-	-	-	-
<i>Sweden</i>	15.19	4.70	5.50	1.80	3.20	15.20	15.200	0.309
<i>Switzerland</i>	1.09	0.16	0.34	0.35	0.23	1.09	1.090	0.150
<i>Ukraine</i>	248.00	97.00	55.00	31.00	65.00	248.00	248.000	0.391
<i>United Kingdom</i>	11.89	3.91	3.68	2.55	1.74	11.89	11.887	0.329
<i>Yugoslavia</i>	4.09	1.20	1.50	0.52	0.87	4.09	4.090	0.293
Europe (total)	2201.47	399.16	412.25	170.00	290.17	1271.58	1357.75	0.285
	Relative potencies ⁴							Average
	1	1	1	1	1			0.285

¹ Officially reported data (EMEP/CEIP-database), except for countries in *italic* (estimates from Gusev et al. 2008).

² Expert estimates from Gusev et al. (2008). BaP = Benzo[a]pyrene, BbF = Benzo[b]fluoranthene, BkF = Benzo[k]fluoranthene, Indeno = Indeno[1,2,3-cd]pyrene.

³ F designates the factor to convert Σ PAH to PAH-eq (benzo(a)pyrene); for BE, BG, DE, NL and ES, for which Σ PAH do not coincide with 'Total 4 PAH', the average F was used to get PAH-eq (based on highest reported emissions).

⁴ Generally, BbF, BkF, and indeno are associated with very low PNEC (Clauson-Kaas et al. 2006, RIVM 1999), because effect data on these compounds are very limited and therefore (unrealistic) high assessment factors are used for estimating the PNEC. In comparison, BaP is the PAHs that benefit from the best effect dataset, and it was therefore chosen to set the relative potencies to 1 in order to express the total PAH releases in terms of BaP equivalents.

Appendix VIII: Emission data for pesticides

Table VIII-1 Data for pesticide use by country ¹

Consumptions (ton/yr)	Fungicide	Herbicide	Insecticide	Others ²	Tot (t)	Notes
<i>Albania</i>	9.40E+01	8.00E+00	1.45E+02	5.80E+01	3.05E+02	1995
Austria	7.37E+02	7.04E+02	4.54E+01	1.35E+01	1.50E+03	
Belarus						
Belgium	1.54E+03	1.51E+03	1.19E+02	4.46E+02	3.62E+03	
Bosnia/Herzegovina						
<i>Bulgaria</i>	9.06E+02	2.49E+03	4.86E+02	1.16E+03	5.04E+03	1992
<i>Croatia</i>	1.41E+03	1.53E+03	1.48E+02	2.49E+02	3.34E+03	1995
Czech Republic	6.77E+02	1.88E+03	1.18E+02	2.52E+02	2.92E+03	DEPA ³
Denmark ³	8.60E+02	2.28E+03	1.21E+02	2.57E+02	3.51E+03	
Estonia	2.11E+01	1.44E+02	2.74E+00	3.00E+01	1.98E+02	
Finland	1.82E+02	7.55E+02	1.71E+01	3.21E+01	9.86E+02	
France	3.40E+04	2.02E+04	1.27E+03	4.82E+03	6.03E+04	
Germany	8.11E+03	1.23E+04	4.93E+02	2.11E+03	2.30E+04	
Greece	3.69E+03	1.14E+03	6.81E+02	3.33E+02	5.85E+03	
Hungary	1.45E+03	3.24E+03	2.73E+02	6.16E+01	5.03E+03	
Ireland	5.37E+02	6.15E+02	5.56E+00	4.34E+01	1.20E+03	
Italy	1.84E+04	5.15E+03	1.52E+03	5.57E+03	3.06E+04	
Kaliningrad region						
Kola Karelia						
Latvia	3.36E+01	1.77E+02	2.89E+00	3.02E+01	2.44E+02	
Lithuania	7.52E+01	3.99E+02	7.56E+00	6.00E+01	5.42E+02	
Luxembourg						
<i>Moldova</i>	6.97E+02	1.18E+03	5.71E+02	9.34E+02	3.38E+03	1993
Netherlands	2.26E+03	2.06E+03	1.38E+02	7.03E+01	4.53E+03	
Norway	5.82E+01	6.03E+01	5.15E+00	4.07E+00	1.28E+02	
Poland	2.59E+03	6.67E+03	3.19E+02	4.31E+02	1.00E+04	
Portugal	1.12E+04	1.65E+03	1.33E+02	2.27E+02	1.33E+04	
<i>Remaining Russia</i>	1.21E+04	1.22E+04	1.69E+03	4.36E+03	3.03E+04	1997
<i>Romania</i>	2.80E+03	3.96E+03	1.11E+03		7.87E+03	2001
Slovakia	3.26E+02	1.01E+03	6.35E+01	3.00E-02	1.40E+03	
Slovenia	2.29E+02	1.44E+02	2.35E+01	4.30E-01	3.97E+02	
Spain	1.66E+04	8.39E+03	2.11E+03	4.14E+03	3.13E+04	
St-Petersburg						
Sweden	2.19E+02	1.56E+03	2.23E+01	4.26E+01	1.84E+03	
<i>Switzerland</i>	6.26E+02	6.27E+02	1.13E+02	2.00E+01	1.39E+03	2004
<i>Ukraine</i>	1.66E+04	3.59E+04	1.42E+04		6.68E+04	1992
United Kingdom	3.78E+03	8.92E+03	3.56E+02	1.62E+03	1.47E+04	
<i>Yugoslavia</i>	2.62E+02	1.49E+02	1.03E+02	1.50E+01	5.29E+02	1998
Total (wo <i>Italic</i>)	1.08E+05	8.10E+04	7.85E+03	2.06E+04	2.17E+05	
Total	1.43E+05	1.39E+05	2.65E+04	2.74E+04	3.36E+05	

¹ For most countries, consumption figures for 2003 were considered (EUROSTAT). For *countries in Italic*, sales were taken from either OECD (2008) or EEA (2004); in this last case, the reported year is referred in the last column.

² The category "Others" include all other types of pesticides (e.g. growth regulators) as well as the few active ingredients for which it has not been possible to allocate a particular use.

³ Consumption data for Denmark are those documented by DEPA (2006); a slight difference can be noted with data from EUROSTAT.

Table VIII-2 Assessed active ingredients, associated with their pesticide class ¹

Active Ingredient	CAS-number	Class ²	Assess. ³
1-naphthyleddikesyre	86-87-3	O	x
2,2-dibrom-2-cyanoacetamid	74070-46-5	H	x
2,3-dihydro-6-methyl-5-phenylcarbamoyl-1,4-oxathiin	67375-30-8	I	x
2-bromo-2-nitropropan-1,3-diol	20859-73-8	F	
3-iodo-2-propynylbutyl carbamat	55406-53-6	F	x
Aclonifen	74070-46-5	H	x
Alpha-cypermethrin	67375-30-8	I	x
Aluminium phosphid	20859-73-8	F	
Amidosulfuron	120923-37-7	H	
Amitraz	33089-61-1	I	x
Asulam	3337-71-1	H	x
Azaconazole	60207-31-0	F	x
Azamethiphos	35575-96-3	I	x
Azoxystrobin	131860-33-8	F	x
Bentazone	25057-89-0	H	x
Betacyfluthrin	68359-37-5	I	x
Bifenthrin	82657-04-3	I	x
Bioresmethrin	28434-01-7	I	x
Bitertanol	55179-31-2, 70585-36-3	F	x
Blodmel	68911-49-9	O	
Borax	1303-96-4	I	
Borsyre (boric acid)	10043-35-3	I	
Brodifacoum	56073-10-0	O	x
Bromadiolon	28772-56-7	O	
Bromoxynil	1689-84-5	H	x
Buprofezin	69327-76-0, 953030-84-7	O	x
Butocarboxim	34681-10-2	I	x
Captan	133-06-2	F	x
Carbendazim	10605-21-7	F	x
Carbofuran	1563-66-2	I	x
Carbosulfan	55285-14-8	I	x
Chloralose	15879-93-3, 76-03-9	O	
Chlorfenvinphos	470-90-6	I	x
Chlormequat-Cl	999-81-5	O	x
Chlorpropham	101-21-3	H	x
Chlorpyrifos	2921-88-2	I	x
Citronellol	106-22-9	I	x
Citrongræsolie			
Clethodim	99129-21-2	H	x
Clodinafop-propargyl	114420-56-3, 105512-06-9	H	x
Clofentezine	74115-24-5	I	
Clomazone	81777-89-1	H	x

Active Ingredient	CAS-number	Class ²	Assess. ³
Clopyralid	1702-17-6	H	x
Coniothyrium minitans	/	F	
Copper dissociated bortset from Copper HDO		F	
Copper HDO	312600-89-8	F	
Copper hydroxycarbonat	12069-69-1	F	
Coumatetralyl	5836-29-3	O	x
Cupricarbonat basisk		F	
Cyanazine	21725-46-2	H	x
Cyazofamid	120116-88-3	F	
Cycloxydim	101205-02-1	H	x
Cyfluthrin	68359-37-5	I	x
Cymoxanil	57966-95-7	F	x
Cypermethrin	52315-07-8	I	x
Cyprodinil	121552-61-2	F	x
Cyromazine	66215-27-8	I	x
Daminozid	1596-84-5	O	x
Dazomet	533-74-4, 556-61-6	I	x
Deltamethrin	52918-63-5	I	x
Desmedipham	13684-56-5	H	x
Diatomejord	61790-53-2	I	
Diazinon	333-41-5	I	x
Dicamba	1918-00-9	H	x
Dichlormat	1966-58-1	H	x
Dichlorprop-P	15165-67-0	H	
Didecyldimethylammoniumchlorid	7173-51-5	F	x
Difenacoum	56073-07-5	O	x
Difenoconazole	119446-68-3	F	x
Difethialon	104653-34-1	O	
Diiflubenzuron	35367-38-5	I	x
Diiflufenican	83164-33-4	H	x
Dimethoat	60-51-5	I	x
Dimethomorph	110488-70-5	F	x
Dinatrium-octaborat	12008-41-2	I	
Dinatrium-tetraborat-decahydrat	1303-96-4	I	
Diquat-dibromid	85-00-7	H	x
Dithianon	3347-22-6	F	x
Diuron	330-54-1	H	x
d-trans-allethrin	584-79-2 (137-98-4)	I	x
Epoxyconazole	106325-08-0, 133855-98-8	F	x
Esfenvalerate	66230-04-4	I	x
Ethephon	16672-87-0	O	x
Ethofumesate	26225-79-6	H	x
Eukalyptusolie	8000-48-4	I	
Fedtsyrer (linoeic acid)	60-33-3		
Fenazaquin	120928-09-8	I	

Active Ingredient	CAS-number	Class ²	Assess. ³
Fenhexamid	126833-17-8	I	
Fenitrothion	122-14-5	I	x
Fenoxaprop-P	71283-80-2	H	x
Fenpropathrin	39515-41-8, 64257-84-7	I	x
Fenpropidin	67306-00-7	F	
Fenpropimorph	67306-03-0	F	x
Fenpyroximate	134098-61-6	I	
Ferriphosphate (ferric phosphate)	10045-86-0		
Ferrosulfate	7720-78-7	F	
Fipronil	120068-37-3	I	x
Flamprop-M-isopropyl	63782-90-1	H	
Flocoumafen	90035-08-8	O	
Florasulam	145701-23-1	H	
Fluazifop-P-butyl	79241-46-6	H	x
Fluazinam	79622-59-6	F	x
Fludioxonil	131341-86-1	F	x
Flupyrsulfuron-methyl	144740-54-5	H	
Fluroxypyr	69377-81-7	H	x
Flurprimidol	56425-91-3	O	x
Foramsulfuron	173159-57-4	H	
Fosetyl-Al	39148-24-8	F	
Fuberidazole	3878-19-1	F	x
Furathiocarb	65907-30-4	I	
Glufosinate-Ammonium	77182-82-2	H	x
Glyphosate	1071-83-6	H	x
Gujaktræolie	8016-23-7		
Haloxypyr-ethoxyethyl	87237-48-7	H	x
Hydroxy isobutyl piperidin carboxylat (picaridin)	119515-38-7	I	
Hymexazole	10004-44-1	F	x
Icaridin			
Imazalil	35554-44-0	F	x
Imidacloprid	105827-78-9, 138261-41-3	I	x
Iodosulfuron-methyl (sodium salt)	144550-36-7	H	
Ioxynil	1689-83-4	H	x
Iprodione	36734-19-7	F	x
Isoborneol	124-76-5		
Kalium oleate (oleic acid)	143-18-0		
Kokosolie	8001-31-8		
Kresoxim-methyl	143390-89-0	F	x
Kuldioxid (CO2)			
Lambda-cyhalothrin	91465-08-6	I	x
Magniumphosphid			
Malathion	121-75-5	I	x
Maleinhydrazid	123-33-1	O	x

Active Ingredient	CAS-number	Class ²	Assess. ³
Mancozeb	8018-01-7	F	x
Maneb	12427-38-2, 96-45-7	F	x
MCPA	94-74-6	H	x
Mechlorprop (MCP)	7085-19-0, 93-65-2	H	x
Mechlorprop-P	16484-77-8	H	x
Mepiquat-chlorid	24307-26-4	O	x
Mercaptodimethur (methiocarb)	2032-65-7	I	x
Mesotrione	104206-82-8	H	
Metalaxyl-M	70630-17-0	F	x
Metaldehyde	9002-91-9, 108-62-3	I	x
Metamitron	41394-05-2	H	x
Metconazole	125116-23-6	F	
Methabenzthiazuron	18691-97-9	H	x
Methopren	40596-69-8, 65733-16-6	O	x
Metribuzin	21087-64-9	H	x
Metsulfuron-M	74223-64-6	H	x
N-(phenylmethyl-1H-purine-6-amine			
Napropamid	15299-99-7	H	x
Natriumsølvthiosulfat		H	
N-cyclohexyldiazoniumdixi-kalium	66603-10-9		
Nellikeolie			
Oxadixyl		F	
Paclobutrazol	76738-62-0	O	x
Paraffin oil			
Pencycuron	66063-05-6	F	x
Pendimethalin	40487-42-1	H	x
Permethrin	52645-53-1, 54774-45-7, 51877-74-8	I	x
Phenmediphan	13684-63-4	H	x
Phlebiopsis gigantea		F	
Phosalone	2310-17-0	I	x
Phoxim	14816-18-3	I	x
Piperonyl-butoxide	51-03-6	F	x
Pirimicarb	23103-98-2	I	x
p-menthan-3,8-diol			
Prochloraz	67747-09-5	F	x
Prochloraz-Mn-Complex	75747-77-2	F	
Propamocarb	24579-73-5	F	x
Propaquizafop	111479-05-1	H	x
Propetamphos	31218-83-4	I	x
propiconazole	60207-90-1	F	x
Propoxur		I	
Propyzamide	23950-58-5	H	x
Prosulfocarb	52888-80-9	H	x
Pyraclostrobin	175013-18-0	F	

Active Ingredient	CAS-number	Class ²	Assess. ³
Pyrethrin I and II	121-21-1, 121-29-9	I	x
Pyridat	55512-33-9	H	x
Pyrimethanil	53112-28-0	F	x
Pyriproxifen		I	
Quinoclamín	2797-51-5	H	x
Rimsulfuron	122931-48-0	H	x
Rotenon	83-79-4	I	x
Simazin	122-34-9	H	x
Spinosad	131929-60-7, 131929-63-0, 168316-95-8	I	
Spiroxamin	118134-30-8	F	
Sulfosulfuron	141776-32-1	H	x
Svovl (sulfur)	7704-34-9	F	x
Tau-fluvalinate	102851-06-9	I	x
Tebuconazole	107534-96-3	F	x
Teflubenzuron	83121-18-0	I	x
Tefluthrin	79538-32-2	I	x
Tepraloxidim	149979-41-9	H	x
Terbuthylazin	5915-41-3	H	x
Thiamethoxam	153719-23-4	F	
Thifensulfuron methyl	79277-27-3	H	x
Thiophanate-methyl	23564-05-8	F	x
Thiram	137-26-8	F	x
Tolclofos-methyl	57018-04-9	F	x
Tolylfluanid	731-27-1	F	x
Triasulfuron	82097-50-5	H	x
Tribenuron-methyl	101200-48-0	H	x
Triflumuron	64628-44-0	I	x
Trifluralin	1582-09-8	H	x
Triforin	26644-46-2, 37273-84-0	F	x
Triflulsulfuron-methyl	126535-15-7	H	x
Trinexapac-ethyl	95266-40-3	H	x
Ylang ylangolie	8006-81-3		

¹ DEPA (2006)

² Several uses can be attributed to some active ingredients: the main one is mentioned. H stands for herbicides, F for fungicides, I for insecticides, O for other pesticides (e.g. growth regulators). It was not possible to characterize all active ingredient use (source: EUROSTAT 2002).

³ Active ingredients, marked with a cross are assessed in the present study (characterization factors available).